VOL. XL. AUGUST, 1908. NO. 2.

AMERICAN

CHEMICAL JOURNAL

[Contributions from the Sheffield Laboratory of Yale University.]

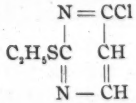
CLVII.—RESEARCHES ON PYRIMIDINES: THE ACTION OF POTASSIUM THIOCYANATE UPON SOME IMIDECHLORIDES.

[THIRTY-FIFTH PAPER.]

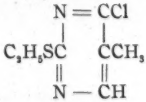
BY TREAT B. JOHNSON AND WALTER F. STOREY.

Two papers entitled "The Action of Potassium Thiocyanate upon Imidechlorides" have previously been published from this laboratory.

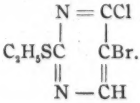
In the first paper[1] the authors showed that the three imidechlorides, *viz.*, 2-ethylmercapto-6-chlorpyrimidine, I., 2-ethylmercapto-5-methyl-6-chlorpyrimidine, II., and 2-ethylmercapto-5-brom-6-chlorpyrimidine, III., reacted with potassium thiocyanate, under certain conditions, giving isothiocyanates. They made no attempts to obtain evidence of the intermediate formation of thiocyanates.



I.



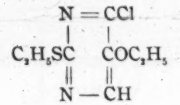
II.



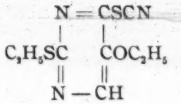
III.

[1] Wheeler and Bristol: THIS JOURNAL, **33**, 448.

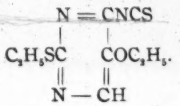
In the second paper,[1] Johnson and McCollum described an unique case of the molecular rearrangement of a thiocyanate into an isothiocyanate. They observed that 2-ethylmercapto-5-ethoxy-6-chlorpyrimidine, IV., reacted, in alcohol, with potassium thiocyanate, giving 2-ethylmercapto-5-ethoxy-6-thiocyanpyrimidine, V., which then underwent a metameric change into 2-ethylmercapto-5-ethoxy-6-isothiocyanpyrimidine, VI.



IV.

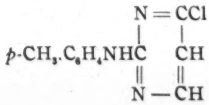


V.

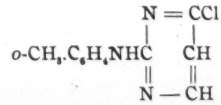


VI.

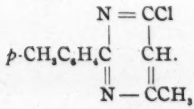
The work described in this paper was undertaken with the object of examining the behavior of potassium thiocyanate towards the three cyclic imidechlorides, *viz.*, 2-paratoluidino-6-chlorpyrimidine, VII., 2-orthotoluidino-6-chlorpyrimidine, VIII., and 2-paratolyl-4-methyl-6-chlorpyrimidine, IX. Incidentally we have also reinvestigated the action of potassium thiocyanate on the imidechlorides, I., II., and III., studied by Wheeler and Bristol.



VII.



VIII.



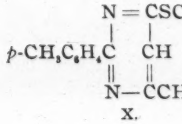
IX.

2-Paratoluidino-6-chlorpyrimidine, VII., and 2-orthotoluidino-6-chlorpyrimidine, VIII., were prepared from 2-ethylmercapto-6-oxypyrimidine. This mercaptopyrimidine reacted, in a smooth manner, with *para*- and *ortho*toluidine, at 100°, giving quantitative yields of 2-paratoluidino-6-oxypyrimidine

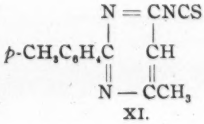
[1] This Journal, **38**, 136.

and 2-orthotoluidino-6-oxypyrimidine, respectively. The oxypyrimidines were then converted into the imidechlorides, VII. and VIII., by treatment with phosphorus oxychloride or phosphorus pentachloride. These two chlorides are more stable in alcoholic solutions than the corresponding 2-ethylmercapto-6-chlorpyrimidine. While the mercapto derivative is decomposed by boiling alcohol the toluidinopyrimidines can be recrystallized repeatedly from this solvent without alteration. We now find that these two chlorides do not react with potassium thiocyanate under normal conditions. They were recovered unaltered after digesting, in alcohol or acetone, with potassium thiocyanate for several hours.

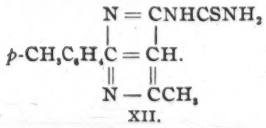
On the other hand, 2-paratolyl-4-methyl-6-chlorpyrimidine, IX., which was obtained from 2-paratolyl-4-methyl-6-oxypyrimidine[1] by the action of phosphorus pentachloride, reacted in a smooth manner with potassium thiocyanate, giving a good yield of 2-paratolyl-4-methyl-6-thiocyanpyrimidine, X. This thiocyanate was stable at ordinary temperature and reacted with thiobenzoic acid, giving a quantitative yield of 2-paratolyl-4-methyl-6-thiopyrimidine. When heated above its melting point, the thiocyanate was converted into a mixture of the isothiocyanate, XI., and apparently a polymeric form of the isothiocyanate melting at 204°. The isothiocyanate reacted with aqueous ammonia at ordinary temperature, giving 2-paratolyl-4-methyl-6-thioureapyrimidine, XII.



X.



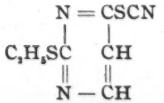
XI.



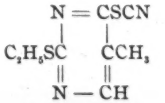
XII.

[1] Glock: Ber. d. chem. Ges., **21**, 2658.

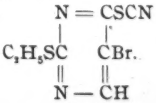
Wheeler and Bristol,[1] in their investigation of the action of potassium thiocyanate on the imidechlorides, 2-ethylmercapto-6-chlorpyrimidine, I., 2-ethylmercapto-5-methyl-6-chlorpyrimidine, II., and 2-ethylmercapto-5-brom-6-chlorpyrimidine, III., worked with the object of converting these chlorides into isothiocyanates. They invariably digested the chlorides with potassium thiocyanate in toluene or alcohol for 3 to 15 hours. Under these conditions the thiocyanates, if formed, would be converted completely into isothiocyanates. We now find that these imidechlorides give practically quantitative yields of the thiocyanates XIII., XIV., and XV., when warmed in alcohol with potassium thiocyanate, if the time of digestion is limited to 20 to 60 minutes. The thiocyanates are stable at ordinary temperature and can be recrystallized from alcohol without alteration. They rearrange smoothly into isothiocyanates when heated above their melting points or when digested for long periods with alcohol. The isothiocyanates, when formed under the latter condition, react with the alcohol, giving the corresponding 6-thiourethanepyrimidines:



XIII.



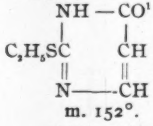
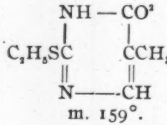
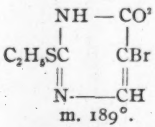
XIV.



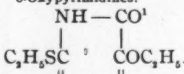
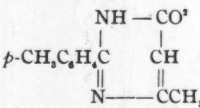
XV.

The melting points and boiling points of all the 6-thiocyanpyrimidines, 6-isothiocyanpyrimidines, and corresponding 6-thioureapyrimidines, which have been prepared in this laboratory, are given in the following table:

[1] *Loc. cit.*

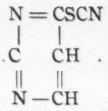
6-Oxypyrimidines.	6-Chlorpyrimidines.	6-Thiocyanpyrimidines.	6-Isothiocyanpyrimidines.	6-Thioureapyrimidines.
 m. 152°.	$C_6H_7N_2S(Cl)$.[2] b_{24} 135°.	$C_6H_7N_2S(SCN)$.[4] m. 82°.	$C_6H_7N_2S(NCS)$.[4] b_{45-50} 200°-205°. $[C_6H_7N_2S(NCS)]_x$.[3] m. 175°.	$C_6H_7N_2S(NHCSNH_2)$.[3] m. 214°.
 m. 159°.	$C_7H_9N_2S(Cl)$.[2] b_{25} 157°.	$C_7H_9N_2S(SCN)$.[4] m. 95°.	$C_7H_9N_2S(NCS)$.	$C_7H_9N_2S(NHCSNH_2)$.[3] m. 192°.
 m. 189°.	$C_6H_6N_2SBr(Cl)$.[2] b_{25} 168°.	$C_6H_6N_2SBr(SCN)$.[4] m. 81°-82°.	$C_6H_6N_2SBr(NCS)$.[4] m. 79°-80°.	$C_6H_6N_2SBr(NHCSNH_2)$.[3] m. 220°.

[1] Wheeler and Merriam: THIS JOURNAL, **29**, 484.
[2] Wheeler and Johnson: *Ibid.*, **29**, 492; **31**, 591.
[3] Wheeler and Bristol: *Ibid.*, **33**, 448.
[4] This paper.

6-Oxypyrimidines.	6-Chlorpyrimidines.	6-Thiocyanpyrimidines.	6-Isothiocyanpyrimidines.	6-Thioureapyrimidines.
 m. 169°.	$C_8H_{11}ON_2S(Cl)$.[1] b_{25} 185°. m. 46°.	$C_8H_{11}ON_3S(SCN)$.[1] m. 66°-67°.	$C_8H_{11}ON_3S(NCS)$.[1] m. 45°-50°.	$C_8H_{11}ON_3S(NHCSNH_2)$[1]. m. 172°.
 m. 216°.	$C_{12}H_{11}N_2(Cl)$.[2] m. 107°.	$C_{12}H_{11}N_2(SCN)$.[2] m. 123°.	$[C_{12}H_{11}N_2(NCS)]_x$.[2] m. 207°-208°.	$C_{12}H_{11}N_3(NHCSNH_2)$.[2] m. 145°-146°.

[1] Johnson and McCollum: THIS JOURNAL, **38**, 136; J. Biolog. Chem., **1**, 437.
[2] *Loc. cit.*
[3] This paper.

EXPERIMENTAL PART.

2-Ethylmercapto-6-thiocyanpyrimidine, 

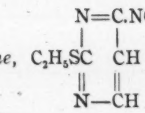
BY DR. E. V. MCCOLLUM.

Three and nine-tenths grams of potassium thiocyanate were dissolved in 40 cc. of 95 per cent alcohol and 7 grams of 2-ethylmercapto-6-chlorpyrimidine added to the solution. There was an immediate reaction with separation of potassium chloride. The mixture was warmed on the steam bath for twenty minutes and the insoluble potassium chloride separated by filtration. On cooling the alcohol solution, the thiocyanate deposited in prismatic crystals which were purified for analysis by recrystallization from alcohol. It separated in aggregates of rectangular prisms melting without effervescence at 82° to a clear oil. The compound was insoluble in alkali and did not react with ammonia or aniline at 100°. Analysis (Kjeldahl):

		Found.		
	Calculated for $C_7H_7N_3S_2$.	I.	II.	III.
N	21.31	20.89	21.32	21.09

When the alcohol filtrates were combined and evaporated to dryness a yellow, crystalline residue was obtained which partially dissolved in cold 10 per cent solution of sodium hydroxide. When this solution was acidified with acetic acid we obtained 0.3 gram of material which crystallized from alcohol in flat prisms or plates melting at 92°–93°. The compound was identical with the 2-ethylmercapto-6-thionethylurethanepyrimidine described by Wheeler and Bristol.[1] A quantitative yield of the above thiocyanate can be obtained by boiling 2-ethylmercapto-6-chlorpyrimidine in acetone solution with potassium thiocyanate. It was very soluble in acetone and separated in prismatic crystals melting at 81°–82°.

[1] *Loc. cit.*

2-Ethylmercapto-6-isothiocyanpyrimidine, 

By Dr. E. V. McCollum.

2-Ethylmercapto-6-thiocyanpyrimidine shows no tendency to rearrange to the isothiocyanate at ordinary temperature. On the other hand, a rearrangement took place when the thiocyanate was heated for 4 to 5 hours at 80°–90°. The isothiocyanate was obtained as an oil which reacted at once with aniline, giving 2-ethylmercapto-6-phenylthioureapyrimidine[1] melting at 205°.

The isothiocyanate was obtained as a yellow oil boiling at 200°–205° (45–50 mm.) when the thiocyanate was distilled. It did not crystallize on standing but a yellow, crystalline compound slowly deposited. This was difficultly soluble in benzene and practically insoluble in alcohol. It melted at 175°–177° and did not react with ammonia. The compound is apparently identical with the product which Wheeler and Bristol obtained by treating 2-ethylmercapto-6-chlorpyrimidine with potassium thiocyanate. It is probably a polymeric form of the isothiocyanate, $(C_7H_7N_3S_2)_x$.

The isothiocyanate reacted at once with aqueous ammonia, with evolution of heat, giving 2-ethylmercapto-6-thioureapyrimidine[2] melting at 214°.

2-Ethylmercapto-5-methyl-6-thiocyanpyrimidine, .—Five grams of 2-ethylmercapto-5-methyl-6-chlorpyrimidine and 3.5 grams of dry potassium thiocyanate were dissolved in 25 cc. of absolute alcohol and the solution boiled for 1 hour. The undissolved potassium chloride was then filtered off and the solution evaporated on the steam bath. We obtained a syrup which was triturated with cold water to remove any potassium chloride and then extracted

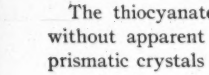
[1] Wheeler and Bristol: *Loc. cit.*
[2] *Ibid.*

with ether. When the ether was evaporated we obtained an oil which did not solidify after standing for several days. This oil partially dissolved in 10 per cent sodium hydroxide. The insoluble portion solidified on standing, and crystallized from 95 per cent alcohol in beautiful prisms melting without effervescence at 95° to a clear oil. It did not react with ammonia or aniline and a nitrogen determination agreed with the calculated value for a thiocyanate (Kjeldahl):

	Calculated for $C_8H_9N_3S_2$.	Found.
N	19.90	19.6

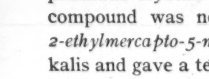
The thiocyanate dissolved at once in cold thioacetic acid without apparent evolution of heat. On standing, beautiful prismatic crystals deposited which melted at 179°–180°. This compound was not examined further but it probably was *2-ethylmercapto-5-methyl-6-thiopyrimidine*. It dissolved in alkalis and gave a test for sulphur.

When the sodium hydroxide solution (above) was acidified with acetic acid we obtained an oil which soon solidified. It was insoluble in water but crystallized from 95 per cent alcohol in stout prisms melting at 90°. It was identical with *2-ethylmercapto-5-methyl-6-thionurethanepyrimidine*,



, which was described by Wheeler and Bristol.[1] A mixture of the two compounds melted at 89°–90°.

2-Ethylmercapto-5-brom-6-thiocyanpyrimidine,



.—This thiocyanate was prepared in the following manner: Five grams of 2-ethylmercapto-5-brom-6-chlorpyrimidine and 2.5 grams of potassium thiocyanate were dissolved in 50 cc. of 95 per cent alcohol and the solution boiled on the steam bath for 20 minutes. The insoluble potassium

[1] *Loc. cit.*

chloride was filtered off and the filtrate cooled, when the thiocyanate deposited in prisms melting at 81°–82°. They were very soluble in acetone, boiling ligroin, warm alcohol, and benzene. The compound did not dissolve in sodium hydroxide and could be warmed with ammonia without alteration. Analysis (Kjeldahl):

	Calculated for $C_7H_6N_3S_2Br$.	Found. I.	II.
N	15.21	15.32	15.28

Action of Thioacetic And Thiobenzoic Acids On 2-Ethylmercapto-5-brom-6-thiocyanpyrimidine:—About 0.3 gram of the thiocyanate was dissolved in a small quantity of thioacetic acid. Reaction took place at once, on warming, without evolution of carbon bisulphide, giving large, well-developed prisms. The compound crystallized from benzene in rhombic prisms that melted at 198° with slight effervescence. It was identified as 2-ethylmercapto-5-brom-6-thiopyrimidine.[1] A mixture of the two products melted at the same temperature. The same 6-thiopyrimidine was obtained when the thiocyanate was warmed in a water bath with a molecular proportion of thiobenzoic acid.

Rearrangement of 2-Ethylmercapto-5-brom-6-thiocyanpyrimidine into the Isothiocyanate:—About 0.2 gram of the thiocyanate was heated for 2 hours at 150°–160°. We obtained a red oil which solidified on cooling and melted at 75°–80°. That a rearrangement had taken place was shown in the following manner: The compound (melting at 75°–80°) reacted at once with ammonia, giving 2-ethylmercapto-5-brom-6-thioureapyrimidine[2] melting at 219°–220°. A mixture of the two preparations melted at the same temperature.

2-Orthotoluidino-6-oxypyrimidine, $o\text{-}CH_3.C_6H_4NH.C(=N)CH.CO.NH$

Eighteen grams of 2-ethylmercapto-6-oxypyrimidine and one molecular proportion of orthotoluidine (14 grams) were heated together on the steam bath for 3 days. The evolution of

[1] Wheeler and Bristol: *Loc. cit.*
[2] *Ibid.*

mercaptan was then complete and a compound was obtained which was difficultly soluble in alcohol. It crystallized from hot alcohol or acetic acid in prismatic crystals melting at 219°–220°. It was soluble in alkali. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}ON_3$.	Found. I.	II.
N	20.89	20.93	20.74

2-Orthotoluidino-6-chlorpyrimidine, $o\text{-}CH_3.C_6H_4NH.C_4N_2H_2Cl$

—Ten grams of 2-orthotoluidino-6-oxypyrimidine were heated on the steam bath with 25 cc. of phosphorus oxychloride until the evolution of hydrochloric acid gas ceased. The excess of phosphorus oxychloride was then distilled under diminished pressure. We obtained a yellow oil, which assumed a crystalline form when treated with ammonia. The compound crystallized from alcohol in corpuscular crystals melting at 78°. It was insoluble in alkali. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{10}N_3Cl$.	Found. I.	II.
N	19.1	18.8	18.92

Action of Potassium Thiocyanate on 2-Orthotoluidino-6-chlorpyrimidine:—Four grams of the chlorpyrimidine and 3 grams of potassium thiocyanate were dissolved in 50 cc. of alcohol and the solution boiled for 2 hours. After filtering a small amount of insoluble material the excess of alcohol was evaporated on the steam bath. We obtained a crystalline residue which crystallized from alcohol and melted at 77°–78°. It responded to a test for chlorine and was identified as the unaltered chloride. Analysis (Kjeldahl):

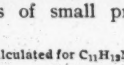
	Calculated for $C_{11}H_{10}N_3Cl$.	Found.
N	19.1	19.07

2-Orthotoluidino-6-aminopyrimidine, $o\text{-}CH_3.C_6H_4NH.C_4N_2H_2NH_2$ — 2-Orthotoluidino-6-chlorpyrimidine

does not react with ammonia at ordinary temperature. When heated with alcoholic ammonia for 2 hours at 140°–150° it gave a quantitative yield of the aminopyrimidine. This was very soluble in alcohol and crystallized from dilute alcohol in aggregates of small prisms melting at 124°. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{12}N_4$.	Found.
N	28.00	27.7

2-Orthotoluidino-6-anilinopyrimidine,



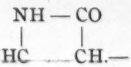
o-$CH_3C_6H_4NHC$ CH.—Three grams of 2-orthotoluidino-6-chlorpyrimidine and 4 grams of aniline were dissolved in 25 cc. of benzene and the solution boiled for 6 hours. It was then filtered and evaporated to dryness. We obtained a crystalline residue which was washed with water to remove aniline hydrochloride and then dissolved in warm dilute hydrochloric acid. The hydrochloride of the anilinopyrimidine crystallized, on cooling, in slender needles melting at 126°. Analysis (Kjeldahl):

	Calculated for $C_{17}H_{16}N_4.HCl$.	Found.
N	17.92	17.73

When the hydrochloride was dissolved in water and ammonia added to the solution the free base separated. It crystallized from dilute alcohol in hexagonal plates melting at 128° to a clear oil. Analysis (Kjeldahl):

	Calculated for $C_{17}H_{16}N_4$.	Found.
N	20.28	20.29

2-Paratoluidino-6-oxypyrimidine, *p*-$CH_3.C_6H_4NHC$ CH.—



This compound is formed, in a smooth manner, by heating 2-ethylmercapto-6-oxyprimidine with a molecular proportion of paratoluidine at 100°. It was difficultly soluble in warm alcohol, acetone, boiling water, and cold acetic acid. It crystal-

lized from acetic acid in clusters of needles melting at 270°–271°. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}ON_3$.	Found.
N	20.89	21.0

2-Paratoluidino-6-chlorpyrimidine, p-$CH_3C_6H_4NH.C_4N_2H_2Cl$.—Twenty-six grams of 2-paratoluidino-6-oxypyrimidine were digested with 65 cc. of phosphorus oxychloride until the evolution of hydrochloric acid gas ceased. We obtained a dark colored solution which was heated at 100° under diminished pressure to remove the excess of phosphorus oxychloride. The residue was dissolved in ice water and the solution made alkaline with ammonia when the chlorpyrimidine deposited. It crystallized from alcohol in prisms melting at 112°–113° to an oil. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{10}N_3Cl$.	Found.
N	19.13	18.99

Action of Potassium Thiocyanate on 2-Paratoluidino-6-chlorpyrimidine:—This pyrimidine was recovered unaltered, melting at 112°–113°, after warming, in acetone solution, with potassium thiocyanate for 2.5 hours.

2-Paratoluidino-6-anilinopyrimidine, p-$CH_3C_6H_4NHC_4N_2H_2NHC_6H_5$.—The hydrochloride of this base was obtained when 2-paratoluidino-6-chlorpyrimidine was warmed in benzene with aniline. The salt was very soluble in hot water and alcohol. It crystallized from alcohol in prisms which decomposed at 134°. Analysis (Kjeldahl):

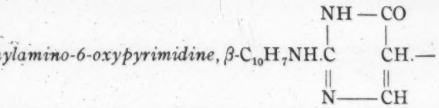
	Calculated for $C_{17}H_{16}N_4.HCl$.	Found.
N	17.92	17.96

When sodium hydroxide was added to an aqueous solution of this salt the pyrimidine base deposited in needles. It was

insoluble in hot water, and crystallized from alcohol in needles melting at 135° to an oil. Analysis (Kjeldahl):

	Calculated for $C_{17}H_{16}N_4$.	Found.
N	20.28	20.15

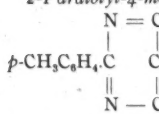
2-β-Naphthylamino-6-oxypyrimidine, β-$C_{10}H_7NH.C_4N_2H_2O$



From β-naphtylamine and 2-ethylmercapto-6-oxypyrimidine. It was insoluble in hot water and difficultly soluble in alcohol. It crystallized from alcohol in clusters of needles melting at 270°. Analysis (Kjeldahl):

	Calculated for $C_{14}H_{11}ON_3$.	Found.
N	17.72	17.77

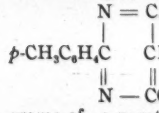
2-Paratolyl-4-methyl-6-chlorpyrimidine,



—This chloride was prepared by heating on the steam bath 15 grams of 2-paratolyl-4-methyl-6-oxypyrimidine[1] with 17 grams of phosphorus pentachloride and about 20 cc. of phosphorus oxychloride for 7 hours. A dark colored solution was obtained which was slowly poured upon crushed ice to destroy the phosphorus halides. The chlorpyrimidine separated at once, and crystallized from alcohol in beautiful prisms melting at 107° to a clear oil. Analysis (Kjeldahl):

	Calculated for $C_{12}H_{11}N_2Cl$.	Found. I.	Found. II.
N	12.81	12.75	12.83

2-Paratolyl-4-methyl-6-thiocyanpyrimidine,



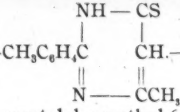
—An alcoholic solution (30 cc.) of 4 grams of 2-paratolyl-4-methyl-6-chlorpyrimidine and 3 grams

[1] *Loc. cit.*

of potassium thiocyanate was boiled for 1.5 hours. The insoluble potassium chloride was removed by filtration, and the solution cooled, when the thiocyanate separated in irregular prisms. It crystallized from alcohol in fern-shaped crystals melting at 123°. When warmed with aniline or aqueous ammonia at 100° it was recovered unaltered. Analysis (Kjeldahl):

	Calculated for $C_{13}H_{11}N_3S$.	Found.
N	17.42	17.2

2-Paratolyl-4-methyl-6-thiopyrimidine,



p-$CH_3C_6H_4C$ CH.—This compound was obtained when 2-paratolyl-4-methyl-6-thiocyanpyrimidine was gently warmed with one molecular proportion of thiobenzoic acid. It deposited from alcohol in slender prisms melting at 114°. Analysis (Kjeldahl):

	Calculated for $C_{12}H_{12}N_2S$.	Found.
N	12.96	12.81

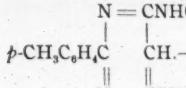
Rearrangement of 2-Paratolyl-4-methyl-6-thiocyanpyrimidine into the Isothiocyanate:—One and five-tenths grams of the thiocyanate were heated, in an oil bath, for 2.5 hours at 130°–135°. We obtained a thick oil which slowly crystallized after cooling. The compound was very soluble in warm alcohol and on cooling crystallized in radiating prisms melting at 207°–208°. It did not react with ammonia and a nitrogen determination agreed with the calculated value for the isothiocyanate. It probably is a polymeric form of the isothiocyanate, $(C_{13}H_{11}N_3S)_x$. Analysis (Kjeldahl):

	Calculated for $(C_{13}H_{11}N_3S)_x$.	Found.
N	17.42	17.35

In a second experiment the thiocyanate was heated for 2 hours at 130°–135°, cooled, and then suspended in aqueous ammonia for 2 days. We obtained a yellow amorphous pro-

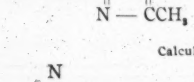
duct which crystallized from alcohol in irregular prisms melting at 145°–146°. A nitrogen determination agreed with the calculated value for

2-Paratolyl-4-methyl-6-thioureapyrimidine,



	Calculated for $C_{13}H_{14}N_4S$.	Found.
N	21.70	21.45

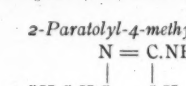
2-Paratolyl-4-methyl-6-aminopyrimidine,



2-Paratolyl-4-methyl-6-chlorpyrimidine was recovered unaltered after heating with alcoholic ammonia for 2 hours at 120° and again for 2 hours at 150°–160°. When heated with ammonia at 180°–190° for 2 hours a good yield of the aminopyrimidine was obtained. It deposited from alcohol in hexagonal tables melting at 178°–179°. Analysis (Kjeldahl):

	Calculated for $C_{12}H_{13}N_3$.	Found.
N	21.10	21.06

2-Paratolyl-4-methyl-6-anilinopyrimidine,



The hydrochloride of this base was obtained when 1 gram of 2-paratolyl-4-methyl-6-chlorpyrimidine and 1 gram of aniline were warmed in benzene for 6 hours. The salt crystallized from alcohol in clusters of needles melting at 269°–270° with effervescence. Analysis (Kjeldahl):

	Calculated for $C_{18}H_{17}N_3$.HCl.	Found.
N	13.48	13.44

The base crystallized from alcohol in needles melting at 120°–121° to an oil. Analysis (Kjeldahl):

	Calculated for $C_{18}H_{17}N_3$.	Found.
N	15.27	15.17

NEW HAVEN, CONN.,
March 1, 1908.

STUDIES ON THE SOILS OF THE NORTHERN PORTION OF THE GREAT PLAINS REGION: NITROGEN AND HUMUS.

BY FREDERICK J. ALWAY AND ROBERT S. TRUMBULL.

In previous articles[1] of this series it has been shown that in many respects the soils of the northern portion of the great plains region resemble those of the arid portions of California. Among the most characteristic features of the latter are the small amount of humus in the surface soil and the very high nitrogen content[2] of the humus. The percentage of nitrogen in the humus of the arid soils of California varies from 9 to 22 per cent, while that of soils from humid regions rarely exceeds six per cent. In the former, the organic matter of virgin soils is present chiefly in the form of humus.

In this article, the term "humus" is used to designate, not the total organic matter of the soil, but only that portion of it which is soluble in dilute alkalies, the "matière noire" of Grandeau.

The analyses reported below were made by the writers while at the Nebraska Wesleyan University, in order to determine whether the generalizations deduced by Hilgard for the soils of California were applicable to the semiarid prairies of Saskatchewan and Alberta. The samples analyzed were not taken with a view to determining their humus content, which accounts for some of them being taken to a depth of less than one foot.

The samples were taken from such widely separated localities, as shown in the fourth column of the table, that they

[1] THIS JOURNAL, **36**, 580; **37**, 1, 275.
[2] Hilgard: Soils, p. 135.

may safely be considered to be typical of the heavier soils of the whole prairie region of the two provinces. The latitude is not given because it differs by less than two degrees between any two of the localities mentioned.

All the samples were of comparatively heavy soil, varying from loam to very heavy clay, except No. 2, which was of fine sand. No. 10 was taken from the surface of a well beaten trail across the prairie. The garden from which No. 12 was taken had received two heavy applications of stable manure although it had been under cultivation only three years.

The percentage of total nitrogen is fairly high in all except No. 2. The percentage of humus is rather low, although much higher than in the arid soils of California. The nitrogen content of the humus does not differ markedly from that of soils from humid regions. The proportion of the total nitrogen of the soil occurring in the form of humus nitrogen is decidedly low, and probably indicates that humification proceeds comparatively slowly in the two provinces.

From the table, it would seem that the surface soil of the semiarid portions of western Canada possesses the characteristics of humid regions while the subsoil[1] shows the marked peculiarities of the subsoils of other arid regions.

[1] This Journal: *Loc. cit.*

No.	Locality.	Province.	Longitude.	Crop at time of sampling.	Depth of sample.	Total N in soil. Per cent.	Humus in soil. Per cent.	Humus N in soil. Per cent.	N in humus. Per cent.	Total N in form of humus N. Per cent.
1	Alameda	Saskatchewan	102°17′	Virgin prairie	0–12 in.	0.18	1.42	0.07	4.93	38.8
2	Carlyle	"	102°17′	"	"	0.10	0.91	0.06	6.59	60.0
3	Indian Head	"	103°40′	"	"	0.28	1.90	0.11	5.79	39.3
4	"	"	"	Western rye grass	"	0.25	2.31	0.13	5.63	52.0
5	"	"	"	Oats	"	0.24	2.45	0.10	4.08	41.6
6	"	"	"	Wheat	"	0.26	1.79	0.09	5.03	34.6
7	"	"	"	"	"	0.22	1.98	0.10	5.05	45.5
8	"	"	"	Summer-fallow	"	0.20	1.02	0.06	5.88	30.0
9	"	"	"	Wheat	"	0.19	1.02	0.06	5.88	31.6
10	Milestone	"	104°29′	Roadway	0–4 in.	0.29	1.85	0.13	7.03	44.8
11	"	"	"	Virgin prairie	0–10 in.	0.19	1.10	0.07	6.36	36.8
12	Belle Plaine	"	105°8′	Garden	0–6 in.	0.30	1.54	0.11	7.14	36.6
13	"	"	"	Virgin prairie	0–12 in.	0.18	0.80	0.05	6.25	27.7
14	"	"	"	"	"	0.22	1.09	0.06	5.50	27.3
15	Moose Jaw	"	105°35′	Summer-fallow	"	0.20	1.29	0.07	5.43	35.0
16	"	"	"	"	"	0.20	1.08	0.06	5.55	30.0
17	"	"	"	Wheat	"	0.20	1.20	0.06	5.00	30.0
18	Lethbridge	Alberta	112°47′	Virgin prairie	"	0.22	1.35	0.08	5.93	36.4
19	"	"	112°51′	"	"	0.20	1.55	0.08	5.16	40.0
20	Gleichen	"	112°54′	"	"	0.22	1.90	0.10	5.26	45.4

LABORATORY OF AGRICULTURAL CHEMISTRY,
UNIVERSITY OF NEBRASKA,
LINCOLN, NEB.

[Contribution from the Kent Chemical Laboratory of the University of Chicago.]

STEREOISOMERIC CHLORIMIDO ACID ESTERS.

By Willis Stose Hilpert.

In 1890 Hantzsch and Werner[1] announced their theory that the stereoisomerism of the benzilmonoximes and dioximes, proved by V. Meyer[2] and his collaborators, and of the aldoximes, proved by Goldschmidt,[3] is caused by the stereochemical properties of the nitrogen present in these substances. Their ideas extended the theory of van't Hoff and Wislicenus, regarding carbon, to nitrogen. They rest upon the assumption that in certain nitrogen derivatives the three valences of the nitrogen atom are directed towards three corners of an irregular tetrahedron, the fourth corner of which is occupied by the nitrogen atom itself. This assumption led directly to the conclusion that the "cis-trans" stereoisomerism of ethylene derivatives (XHC = CHX) might also occur in certain cases when a double bond exists between nitrogen atoms or between a carbon and a nitrogen atom, as in the case of oximes of the type

$$\begin{array}{l} R-C-R' \\ \quad\| \\ N-X \end{array} \qquad \text{and} \qquad \begin{array}{l} R-C-R' \\ \quad\| \\ X-N. \end{array}$$

Hantzsch and Werner's theory has proved remarkably fruitful and reliable in explaining the occurrence of stereoisomerism among such derivatives as the oximes, the hydrazones, and diazo bodies, and must be considered as firmly established. If there has been any criticism at all attaching to the theory, it has lain in the unusually large proportion of negative results incidental to efforts to vary the radical X in the above type from the form which it has in the oximes (X = OH; OR'; O — acyl) and hydrazones (X = NHC_6H_5; NRC_6H_5; N — acyl — C_6H_5).

We possibly have some stereoisomeric phenylimide derivatives, but the occurrence of such stereoisomers as claimed

[1] Ber. d. chem. Ges., **23**, 11, 1243 (1890).
[2] *Ibid.*, **16**, 503, 1616, 2176 (1883).
[3] *Ibid.*, **22**, 3113 (1889).

by Schall[1] for modifications of carbodiphenylimides has been challenged; and similarly v. Miller and Plöchl's[2] assumptions of stereoisomerism for certain condensation products of the aldehydeamines have been questioned as not excluding rigorously enough the possibility of structural isomerism. Hantzsch's[3] efforts to obtain stereoisomers in which X was C_6H_5 and other radicals proved fruitless. These negative results have justly been considered as showing the extreme tendency of such compounds to persist in one, the more stable, of a pair of possible stereoisomeric forms. It has, however, always been considered of theoretical importance to obtain stereoisomeric compounds in which X should be as simple as possible and thus limit the cause of the stereoisomerism, experimentally, rigorously to the doubly bound nitrogen and carbon atoms, as it is in the theory. This missing link, fully confirming Hantzsch and Werner's views, was discovered in 1903 by Stieglitz and Earle[4] in the course of investigations concerning the "Beckmann Rearrangement," in which they obtained stereoisomeric methyl chlorimido-*m*-nitrobenzoates, $m\text{-}NO_2C_6H_4C(:NCl)OCH_3$.

In a later investigation carried out with Dr. W. Hale, Stieglitz[5] prepared a second pair of stereoisomers of the corresponding ethyl ester, although only exceedingly small quantities of the one form were obtained; and, in particular, it was discovered that in either of the above cases the less stable stereoisomer can be readily converted into the more stable one by chemical means, namely, by the action of chlorine, the very reagent which one would anticipate as capable of effecting such a transformation.[6]

Only two pairs of such stereoisomers being known, the one form in this case being obtained only in very small quantities, Professor Stieglitz suggested to me to try to discover further representatives of this kind and, in particular, to put

[1] Schall: Z. physik. Chem., **12**, 145 (1893); Ber. d. chem. Ges., **25**, 2883 (1892); J. prakt. Chem., **53**, 149 (1896).

[2] V. Miller and Plöchl: Ber. d. chem. Ges., **25**, 2031 (1892).

[3] *Ibid.*, **25**, 977 (1895); **30**, 3003 (1897); **34**, 822 (1901).

[4] This Journal, **30**, 399 (1903).

[5] The results will be published soon.

[6] See Stieglitz: This Journal, **40**, 42 (1908).

each pair to a rigorous test regarding the proof of the identity of structure and the exclusion of the occurrence of mere physical or crystal isomerism. The results of this investigation, as carried out under his direction, are found in this paper. It may be stated at once that I have obtained five further pairs of stereoisomeric chlorimidoesters, for each of which structural and crystal isomerisms were rigorously excluded, and, that, in fact, stereoisomers were obtained in all but two cases, where a solid chlorimidoester resulted from the action of hypochlorous acid on an imidoester. The five new pairs of stereoisomers are:

Methyl chlorimido-*p*-nitrobenzoate,

$$p\text{-}NO_2C_6H_4C(:NCl)OCH_3;$$

Ethyl chlorimido-*p*-nitrobenzoate,

$$p\text{-}NO_2C_6H_4C(:NCl)OC_2H_5;$$

Methyl chlorimido-*p*-methyl-*m*-nitrobenzoate,

$$m\text{-}NO_2\text{-}p\text{-}CH_3C_6H_3C(:NCl)OCH_3;$$

Methyl chlorimido-β-naphthoate, $C_{10}H_7C(:NCl)OCH_3$;

Ethyl chlorimido-β-naphthoate, $C_{10}H_7C(:NCl)OC_2H_5$.

No stereoisomers were obtained in the case of methyl chlorimido-*p*-brom-*m*-nitrobenzoate, and methyl chlorimido-*p*-brombenzoate. The identity of structure was proved in each of the above cases by the action of dry hydrogen chloride, which regenerated from each of the two members of the pair the imidoester hydrochloride that was used in preparing the chlorimides. The imidoester salt was identified by the action of water, leading to an acid ester of a characteristic melting point. The two samples of acid esters obtained from the pair of stereoisomers not only give the same melting point alone, but also give the same melting point when mixed with each other. The actions are as follows:

$$RC(:NCl)OR' + HCl \rightleftarrows RC(NH_2Cl)OR' + Cl_2;$$

$$RC(NH_2Cl)OR' + H_2O \rightleftarrows RCOOR' + NH_4Cl.$$

The result proved beyond any doubt that R has the same structure in each of a pair of stereoisomers (for instance, in

regard to the position of a nitro group) and that the group C(:NCl)OR′ also is identical in structure in the pair of isomers. The hydrochloride of the imidoester, when heated, gives an alkyl halide and an acid amide, according to the formulation

$$RC(NH_2Cl)OR' \longrightarrow RCONH_2 + R'Cl.$$

When the acid amide was thus prepared from each of a pair of stereoisomers, it proved to be the same in both cases.

The possibility of having polymeric forms was excluded by the results of molecular weight determinations carried out with two pairs of the above list of stereoisomeric bodies, the simple molecular weight being found in each instance, as was the case in the work of Stieglitz and Earle.

Physical or crystal isomerism was excluded by the fact that each of every pair of stereoisomers maintained its own identity in all changes of physical condition—each crystallizing unchanged from solvents, irrespective of differences of solubility; each crystallizing unchanged after being melted, solidifying unchanged even in contact with a crystal of the other form. In every instance each depresses the other's melting point, usually very considerably; the two forms thus showed complete physical independence of each other. In addition to these methods, which have been employed by Stieglitz and Earle, I was able to prove also that the two stereoisomeric methyl chlorimido-*p*-nitrobenzoates maintain their identity also as gases, each crystallizing, after evaporating *in vacuo*, wholly in its own characteristic form, of characteristic melting point. In fact, under no circumstances was a single transformation observed of one form into the other by physical methods.

So much the more impressive is the fact that, in the case of the first three pairs of stereoisomers mentioned above, it was found possible to transform the less stable stereoisomer into the more stable one by the action of chlorine on the fused chlorimide, the action lasting only two minutes. The explanation given for this transformation[1] suggested at once that it might be reversible to some extent. I was able to

[1] Stieglitz: *Loc. cit.*

bring the complete experimental proof of this anticipated fact in two cases tried, *viz.*, for the two methyl chlorimido-*m*- and *p*-nitrobenzoates, respectively. Chlorine, acting on the naphthalene derivatives, gave gummy products, probably formed by the action of chlorine on the naphthalene nucleus. I found, however, that boiling water transforms one stereoisomer into the other in this series, and that here too the action is a *reversible one*. The water acts probably by means of traces of chlorine or hypochlorous acid formed from the chlorimide used.

There is no question, then, that the five pairs of chlorimides listed above are true stereoisomers of the "syn" and "anti" type of compounds of Hantzsch and Werner, *viz.*,

$$\underset{\text{(Syn)}.}{\begin{matrix} R{-}C{-}OR' \\ \| \\ ClN \end{matrix}} \quad \text{and} \quad \underset{\text{(Anti)}.}{\begin{matrix} R{-}C{-}OR' \\ \| \\ NCl \end{matrix}}.$$

Scarcely any clews have been obtained as to which of each pair should be given the "anti" and which the "syn" configuration. Stieglitz and Hale[1] found in the case of methyl chlorimido-*m*-nitrobenzoate that both pairs suffer to a certain extent a "Beckmann Rearrangement" by destructive distillation above 200°, and their quantitative experiments showed that there is no essential difference in this respect between the two forms. At lower temperatures the compounds are very stable, excepting towards reagents reducing the chlorimido group and thus destroying the cause of stereoisomerism. The only clew of any value regarding the configuration lies in the following observations: Both for methyl chlorimido-*m*-nitrobenzoate, as found by Stieglitz and Earle, and for methyl chlormido-*p*-nitrobenzoate, as I have found, the *more stable*, so-called β form crystallizes in characteristic plates, has a lower melting point, and is more soluble than the α form, which crystallizes in needles. The β form is readily formed from the α body by the action of chlorine and is always the chief product of the reaction between hy-

[1] Unpublished reports.

pochlorous acid and the free imidoester. Now in both series, for the meta- as for the paranitro acid, the conditions as to stability and yield are absolutely reversed when chlorimido *ethyl* esters are prepared. The stereoisomers crystallize again in characteristic plate and needle forms, but the higher melting needle form (α) is the more stable, and is almost exclusively formed; and the lower melting plate form (β) goes readily over to the needle form (α) by the action of chlorine. This marked change of stability in going from the methyl to the ethyl ester is best explained by the assumption that the β forms have the "anti" configuration,[1] as given above, and that the substitution of the larger ethyl radical for methyl—which should not reverse any condition for chemical or other than physical reasons—crowds out the chlorine atom and makes the "syn" derivatives, by reason of stereochemical considerations, the more stable. It may be added that Werner[2] found that of two stereoisomers of methyl oximidobenzoate, which correspond to our chlorimides, the "anti" form is the more stable one; the "syn" form, crystallizing in needles, goes over readily into the "anti" form:

$$\begin{array}{l} C_6H_5—C—OCH_3 \\ \quad\quad\| \\ \quad\quad N—OH \end{array}$$

Anti (stable).

$$\begin{array}{l} C_6H_5—C—OCH_3 \\ \quad\quad\| \\ \quad\quad HO—N \end{array}$$

Syn (unstable), needles.

This agrees with the above decisions in regard to the chlorimido methyl esters, *viz.*,

$$\begin{array}{l} m\text{- or } p\text{-}NO_2C_6H_4C—OCH_3 \\ \quad\quad\quad\quad\| \\ \quad\quad\quad\quad N—Cl \end{array}$$

β or anti (stable), plates.

and

$$\begin{array}{l} m\text{- or } p\text{-}NO_2C_6H_4C—OCH_3 \\ \quad\quad\quad\quad\| \\ \quad\quad\quad\quad Cl—N \end{array}$$

α or syn (unstable), needles.

Both the ethyl oximidobenzoates appear to be stable, and neither form, it seems, has as yet been converted into the other.

In the case of the stereoisomeric chlorimidonaphthoates the evidence for determining the configurations is less pronounced, the crystal forms being much alike and no such very decided

[1] "Anti" in regard to the acid radical R.

[2] Ber. d. chem. Ges., **29**, 1158 (1896).

differences in stability of the stereoisomers being apparent. But still we have the same contrasts as in the pairs discussed. Of the *methyl* chlorimidonaphthoates, the lower melting, more soluble form (β) is the chief product of the action, although a fair yield of the higher melting α form is also obtained. In the case of the ethyl esters, the condition is again reversed; the higher melting, less soluble α form is again obtained in larger quantity. So it is very probable that in these two cases, as in the previous ones, the higher melting α bodies have the "syn" configuration, and the lower melting β forms have the "anti" configuration, the "anti" configuration being less favored by the lengthening of the alkyl from methyl to ethyl.

These configurations are given simply in a *preliminary* way; further facts will be needed to establish them conclusively.

Repeated attempts were also made by me to prepare stereoisomeric pairs of *bromimidoesters*, methyl imido-*m*-nitrobenzoate and β-naphthoate being used for the purpose; but all the attempts were futile. It is impossible to say whether these negative results are due to the greater mass of the bromine atom and consequent greater stereochemical interference with the existence of the one stereoisomer,[1] or rather to the fact that bromimidoesters are much less stable substances and that any free bromine liberated by the action of traces of hydrobromic or any other acid would, like chlorine, rapidly change the less stable to the more stable stereoisomer. We are inclined to consider the latter the chief reason for the formation of only one stereoisomer.

In the following pages the most important experimental results will be given. As the isolation of such sensitive stereoisomers is dependent on the careful observations of nice precautions, and the rigorous proof of stereoisomerism lies in the conscientious, exact exclusion of the possibilities of structural and physical isomerism and polymerism, it has been thought best to give the experimental data, when necessary, very explicitly and in detail. This has seemed the more

[1] Victor Meyer showed in his work on stereochemical interference with esterification and saponification that bromine atoms interfere more than chlorine atoms do.

imperative as in a number of cases apparent crystal isomerisms were also observed, *simulating the stereoisomers*, but fundamentally different from them when critically investigated.

EXPERIMENTAL PART.

α and β Methyl Chlorimido-m-nitrobenzoate, $NO_2.C_6H_4C(Cl{=}N){-}OCH_3$ α, and $NO_2C_6H_4C(N{=}Cl){-}OCH_3$ β.—These two esters formed the first pair of stereoisomeric chlorimidoesters prepared by Stieglitz and Earle.[1] The study of these bodies was continued by me principally in order to determine, more precisely than had been done, the best quantitative conditions for obtaining a maximum yield of the less stable stereoisomer, the α body; and also in order to work out exactly the best method for a roughly quantitative separation of the two isomers.

In the first experiments, solutions of sodium hypochlorite[2] were used to convert the imidoester salt into the chlorimide, from one to nine molecules of hypochlorite being used. The products obtained were often impure, occasionally oily, refusing to crystallize, and some were colored. It was suspected that the excess of free alkali in the hypochlorite mixture prepared in this way reversed the reaction with the chlorimide, and, by suppressing the free hypochlorous acid, also interfered with the formation of the chlorimide. For these reasons it was thought advisable to use *free* hypochlorous acid, prepared from sodium carbonate and chlorine according to Erlenmeyer,[3] in order to secure, in a solution as little acid as possible, the maximum amount of free hypochlorous acid. One molecule of chlorine was allowed to react on one molecule of sodium carbonate at 0°. When this mixture was ready, the hydrochloride of the imidoester was rapidly dissolved in a little cold water, immediately treated with a solution of two molecules of potassium bicarbonate, and this mixture added at once to the hypochlorous acid solution. The excess of potassium

[1] THIS JOURNAL, **30**, 401 (1903).
[2] Prepared according to Graebe: Ber. d. chem. Ges., **35**, 2750 (1902).
[3] Ann. Chem. (Liebig), **219**, 185.

bicarbonate was used to weaken the acidity of carbonic acid by the presence of an excess of its salt ions.

The first attempt made in this way, three molecules of hyprochlorous acid being used, gave a beautiful, granular product, free from any suggestion of oil or other impurities. By the method of fractionation given below 11.4 per cent (referred to the total crude yield) of α body, melting at 86°, was obtained.

When borax was added with the potassium bicarbonate, with the object of keeping the solution still more nearly neutral, an 8 per cent yield of the α form was obtained.

A 25 per cent yield of the α body was obtained by using a smaller excess of hypochlorous acid, namely, two molecules.

Finally, hypochlorous acid was also prepared by passing chlorine into a suspension of mercuric oxide in water. In one experiment, in which three molecules of acid prepared in this way were used, a yield of 16 per cent of the α body was obtained.

From the results of the above experiments it was obvious that the use of two molecules of hypochlorous acid gave the best yield of the α body, and accordingly this method was adopted in preparing larger quantities of the α modification. The proportions used are as follows: For each gram of the imidoester salt, 3 grams crystallized sodium carbonate and 0.33 gram chlorine were used for the preparation of the hypochlorous acid, and one gram potassium bicarbonate to liberate the imidoester.

In connection with the preparation of larger quantities of the α body, experiments were also made on a roughly quantitative method for separating the α and β forms. Stieglitz and Earle[1] found the α body to be quite soluble in chloroform and hardly soluble in cold ligroin, and so used this as a method for separation, but they do not give any definite proportions of chloroform and ligroin used with a weighed amount of the chlorimide.

The α modification (0.1 gram) was dissolved in 0.5 cc. of chloroform, and 2 cc. ligroin were added, giving a precipitate of needles. Further addition of ligroin gave no more precipi-

[1] *Loc. cit.*

tate. The precipitate weighed 0.08 gram and melted at 86°–87°. This showed that the α body is almost entirely thrown out of such a chloroform solution by ligroin. One tenth gram of pure β body was dissolved in 0.5 cc. chloroform and gave no precipitate at all on the addition of 2 cc. of ligroin.

One tenth gram of the α body with 0.2 gram β form, dissolved in 1.5 cc. chloroform, were precipitated with 9 cc. of ligroin. The precipitate weighed 0.05 gram and melted at 86°–87°.

From a solution of 0.1 gram α with 0.2 gram β body in 0.5 cc. chloroform, 2 cc. of ligroin gave a precipitate, 3 cc. giving a trace more—altogether 0.15 gram—melting at 66°, and at 61° when mixed with an equal part of the pure α body. The melting points show that the precipitate had a considerable quantity of β form present, and that the proportion of chloroform must not be reduced.

The best method, then, for separating the chlorimides from a crude yield is to use 0.5 cc. of chloroform for each 0.1 gram of the crude chlorimides, and to add four to five volumes of ligroin. These proportions give the best results as to yield and purity of the α form, and they were used in the experiment giving the largest yield of α body, *viz.*, 25 per cent of the crude yield.

For the preparation of the β form on a large scale, it is best to convert most of the α body in the crude mixture into the β compound by the action of chlorine (see below), and then to fractionate the product by precipitating from a chloroform solution as much of the α body as possible and allowing the mother liquor to evaporate. This leaves the β body in a very pure form. A final method of purification of the β form that proved successful consisted in dissolving the almost pure body in very little slightly warm chloroform (less than 0.5 cc. per 0.1 gram chlorimide) and adding seven volumes of ligroin. Only part of the β body is precipitated by this method, but it is perfectly pure.

The Transformation of the Labile α Compound into the Stable β Body—A Reversible Reaction.—As proved by Stieglitz and Earle, the two stereoisomeric chlorimides are not changed from one form to the other by any physical means. Stieglitz and

Hale,[1] however, succeeded in transforming the α compound into the β body by chemical means, *viz.*, by the action of chlorine. At 90° the transformation is accomplished in one or two minutes; at ordinary temperatures and in chloroform solution only very slowly.

The explanation of this transformation[2] suggested at once that the change ought to be, to a certain extent, a reversible one. To test this view, I allowed chlorine to act separately on absolutely pure α and pure β methyl chlorimidometanitrobenzoates at 90°. Both bodies, especially the β form, were first carefully tested by the same method of fractionation that was to be used after the action of chlorine, and found to be absolutely pure and free from the other isomer.

Pure chlorine, made from potassium permanganate and concentrated hydrochloric acid, was carefully washed with moist beads to free it from traces of acid and then carefully dried by passing it through two tubes of beads wet with concentrated sulphuric acid. The gas, thus treated, was allowed to fill a flask containing 0.2 gram of the pure α body, which was then heated to 90° for two minutes. The α body melted at this temperature and remained liquid during the process. After the action had proceeded for two minutes the substance was cooled and freed from chlorine vapors. The resulting substance melted at 73°–84°, leaving a residue which did not melt.

The whole was then dissolved in as little chloroform as possible and an excess of ligroin added; this gave a slight precipitate of a high melting body, probably a trace of regenerated hydrochloride. The mother liquor of the imidoester, on evaporating, gave crystals on the sides and bottom of the beaker, melting at 81°–82° and 83°–84°, respectively. With equal parts of the α body they melted at 61°–63°, the depression of the melting point showing that no α body was present. With equal parts of the β body the crystals melted at 82°. This showed conclusively that the crystals were the β form. The form of the crystals, as plates, confirmed this conclusion.

[1] Unpublished results.

[2] Stieglitz: THIS JOURNAL, **40**, 42 (1908).

So, with the exception of the small amount of high melting body, almost all the α body was converted into the β compound.

Half a gram of absolutely pure β body was treated with pure, dry chlorine at 90° for two minutes. The flask was cooled, the chlorine withdrawn, the residue dissolved in 3 cc. of chloroform, and 25 cc. ligroin were added, giving a precipitate similar to that found after the treatment of the α form. The mother liquor gave large plates identical with the β plates, along with smaller crystals on the sides of the beaker. These smaller crystals, weighing 0.135 gram, were dissolved in 0.5 cc. of chloroform and 3 to 4 cc. of ligroin were added. A precipitate was thrown down when the beaker was scratched with a glass rod. Alone, it melted at 84°; mixed with some pure β form, the mixture melted also at 84°, showing the new substance to be identical with the β body.

The crystals from the second mother liquor—only a small amount—melted at 65°–67°. There were enough, however, for analysis by potassium iodide, acid, and sodium thiosulphate for the chlorine content.

0.0254 gram substance gave 0.0041 gram chlorine.

	Calculated for $C_8H_7O_3N_2Cl$.	Found.
Cl	16.52	16.42

This analysis shows that the crystals melting at 65°–67° were pure methyl chlorimido-*m*-nitrobenzoate. Since, then, the crystals were pure and yet had the melting point 65°–67° characteristic of a mixture of the α and β bodies, they must have consisted of such a mixture.[1] We are justified in concluding, then, that some α compound was actually formed by the action of chlorine on the β body.

As the previous experiment proved that after the action of chlorine at 90° the α form would be present only in exceedingly small quantities, the reversal of the action was again attempted in the following way: The α body, if formed, was to be removed as completely as we could, with the minimum possible amount of β body, and the main quantity of the β compound treated repeatedly with chlorine, the α form being continually removed.

[1] Stieglitz and Earle: *Loc. cit.*

Absolutely pure β crystals (melting at 83°–84) were treated with pure dry chlorine for two minutes at 90°. The flask was cooled, freed from chlorine, and the contents extracted with 10 cc. cold ligroin, the ligroin and its vapors removed, the residue again treated with chlorine and again extracted, etc. In this way four extracts were made after four treatments with chlorine; each extract was allowed to evaporate to dryness and gave needles, plates, and mixed crystals.

The needles and mixtures, looking more promising, because of their crystalline form, were examined for the presence of the α body. They were dissolved in very little chloroform and precipitated with ligroin, as usual in obtaining the α form. After a short time a precipitate appeared, which was filtered, washed with ligroin, and dried. The melting point, 86°–87°.5, indicating the presence of the pure α body, its identity was confirmed by the melting point of a mixture of the body with added β body—the melting point was depressed to 62°–63°. Thus the formation of the α form from the β form was established.

Likewise, crystals from the mother liquor of the α precipitate melted at 87°–88°, and mixed with pure α body melted at 85°–87°, showing conclusively again that the crystals above were the α compound. Therefore, by these experiments, it is proved that the action of chlorine on the chlorimides is a reversible reaction.

The Constitution of the Stereoisomers.—It was thought best to confirm the constitution of the α body, as my products were obtained from new preparations of *m*-nitrobenzonitrile entirely distinct from those of Stieglitz and Earle. The same method employed in Stieglitz's and Earle's work was used. One tenth gram pure, dry α body was treated with dry hydrogen chloride in ligroin. This resulted in the formation of a white precipitate of the hydrochloride of methyl imido-*m*-nitrobenzoate. It was filtered, washed with ligroin, and then dried. Part of it was heated to 120° and gave methyl chloride and *m*-nitrobenzamide, melting sharply at 142°. The second part of the hydrochloride was treated with water; it was dissolved to a clear liquid, then in a short time a cloudy precipitate of methyl *m*-ni-

trobenzoate was formed by the decomposition of the imidoester salt. The melting point of the precipitate, 77°–78°, proved the identity of the ester.

These experiments showed that in the α body obtained the methyl group is really attached to the oxygen of the acid radical, and that the nitro group is in the meta position in the benzene radical.

Similarly the constitution of the pure β body was again proved rigorously; it also gave metanitrobenzamide, melting at 140°, and the methyl ester of *m*-nitrobenzoic acid (m. p. 78°), as in the experiment with the α body.

From the experiments it is evident that the bodies worked with have exactly the same structure, that of a methyl ester of chlorimido-*m*-nitrobenzoic acid, and that they must be stereoisomeric chlorimido compounds.

Stereoisomeric Methyl Chlorimidoesters of p-Nitrobenzoic Acid,

$NO_2C_6H_4C(=NCl)OCH_3$ and $NO_2C_6H_4C(=N)OCH_3.Cl$

α (syn), needles. β (anti), plates.

The next body examined for the existence of stereoisomers was methyl chlorimido-*p*-nitrobenzoate.

The nitrile for the preparation of the imidoester salt was obtained from Kahlbaum's *p*-nitrobenzoic acid, m. p. 141°, by successive treatment with phosphorus pentachloride, concentrated ammonium hydroxide, and phosphorus pentoxide. The nitrile was distilled with steam and was found, by its melting point, 147°, to be pure.

The imidoester salt was obtained best from a benzene solution of the nitrile and one and one-tenth molecules of methyl alcohol. The free imidoester was made by liberating it from the aqueous solution of the salt by potassium bicarbonate. It proved to be a white, crystalline body, melting at 93°–94° and readily soluble in hydrochloric acid.

For the preparation of the chlorimide the salt was dissolved in water and twice the calculated amount of potassium bicarbonate solution added. This mixture, containing the free

base, was at once poured into a cold solution of twice the calculated amount of free hypochlorous acid, prepared from chlorine and sodium carbonate. The chlorimide separated immediately, but to give the reaction time to complete itself the mixture was vigorously shaken for several minutes. Then the product was brought on a Hirsch funnel, washed with cold water, and quickly brought on a clay plate.

As a preliminary purification, the chlorimide was dissolved in acetone, in which it is extremely soluble, and reprecipitated by water. The product thus obtained melted at 54°.

A large quantity of the chlorimide was carefully fractionated by the addition of ligroin to the chloroform solution. The chlorimide (2.44 grams) was dissolved in 12 cc. of chloroform, and 40 cc. of ligroin were added. A white, crystalline precipitate resulted, melting at 95°–98°; mixed with some of the plate material (m. p. 76°, see below), it melted below 60°–61°. This characteristic depression of the melting point pointed sharply to the presence of two stereoisomeric bodies.

From the mother liquor of the precipitate, large plates formed, melting at 76°. In the endeavor to get larger yields of the α body, several experiments were made. First 6 times, then 1.25 times the calculated amount of hypochlorous acid was used; thirdly, the hypochlorous acid was warmed to 30°–35°. In no case was the yield of the α body improved. Several more preparations were then made with two molecules of hypochlorous acid in order to get larger amounts of the high melting needles and the low melting plates. The former were repeatedly refractionated by solution in chloroform and precipitation by ligroin, giving, as the highest melting point, 99°–100°. Further fractionation failed to change this melting point, and, as was done in the meta series, the name α body was given to this compound, as the higher melting form.

The other form, crystallizing in plates, gave the constant melting point 76°; it was called the β form. Its crystal form resembles closely that of the β body of the metanitrobenzoate series. It was obtained pure by selecting the clearest looking plates from the crystals left by evaporation of the mother liquors, from which the α form had been precipitated. These

plates were redissolved in a minimal quantity of chloroform and four or five volumes of ligroin added, thus leaving the last traces of the α body in solution and precipitating the β compound, melting at 76°.

A mixture of the two pure crystal varieties invariably melted much lower than either form, usually near 60°.[1]

That these two bodies, with different crystal forms and melting points 24° apart, are stereoisomers rests again on the proof of (*a*) the identity of their analytical composition; (*b*) the identity of their structure; (*c*) the persistence of their separate identity under different physical conditions; and (*d*) the transformation of one into the other by a rearrangement by means of chlorine.

Upon analysis the following results were obtained:

I. 0.1228 gram substance (α body) gave 0.0200 gram Cl.

II. 0.1486 gram substance (β body) gave 0.0241 gram Cl.

	Calculated for $C_8H_7O_3N_2Cl$.	Found. I.	II.
Cl	16.52	16.34	16.27.

These analyses show, then, that as far as empirical composition is concerned, the two bodies have the formula $C_8H_7O_3N_2Cl$.

The identity of structure of the two compounds was proved exactly as in the meta series; namely, by converting each compound back to the imidoester salt, and getting from each the same *p*-nitrobenzamide and *p*-nitrobenzoic methyl ester. Eleven hundredths gram of the pure α body in ligroin was treated with dry hydrogen chloride. The hydrochloride of the imidoester thus formed gave *p*-nitrobenzamide (m. p. 192°–195°) and methyl *p*-nitrobenzoate, which melted at 92°–95°. The melting point of methyl *p*-nitrobenzoate is given as 96°.

To complete the proof of identity, some synthetically prepared methyl *p*-nitrobenzoate was mixed with that prepared above. The mixture melted at 94°–96°, showing that the two bodies are identical.

In exactly the same way, the β body was carried through the process of reversion to the imidoester salt, which gave, under

[1] Approximately equal quantities were mixed for all such tests in this investigation.

treatment by heat, *p*-nitrobenzamide, m. p. 192°–195°; and by water the methyl *p*-nitrobenzoate, m. p. 93°–94°; a mixture with the ester obtained from the α body melted at the same point.

These experiments prove the perfect identity in structure of the α and β forms of methyl chlorimido-*p*-nitrobenzoate, the reactions involved being absolutely the same for both forms and leading to identical products.

The possibility of the needles (α) and the plates (β) being physical isomers or crystal modifications is rigorously excluded by their physical behavior. One form is never converted into the other by the action of physical solvents or by physical contact in solution or in a liquid condition. The α form, melted at 100°, and allowed to cool and solidify, melted again at precisely 100°. The plates melted at 76°, and allowed to solidify, melted again exactly at 76°. A mixture of the two, as has been stated, melts at 60°–61°, and after the mixture has solidified it melts again at 60°–61°, which shows that the two forms preserve their identity even when fused and crystallized together.

A concentrated solution of the pure β body in chloroform gives, on the addition of ligroin, a precipitate of the pure β modification, although the α form is the less soluble of the two and, if present in more than very small quantities, is precipitated first. The two forms preserve their identity, therefore, not only in the solid condition but in the molten and dissolved substances.

Finally the persistence of each form even in the gaseous condition was established as follows: 0.1 gram of the pure α body was heated in a test tube fitted with an inner condensing tube placed about 1 cm. above the substance in order to avoid any decomposition by overheating the compound, since any acid fumes would have evolved chlorine which, in turn, would have caused a rearrangement of the stereoisomers (see below). At 1 mm. pressure boiling commenced at 130°, and soon a sublimate appeared on the sides of the inner tube. After cooling, the sublimate was found to melt at 98°–99°, and mixed with pure α body again melted at 98°–99°, which shows that

even in the gaseous form no change into the β body takes place, the α molecules preserving their identity absolutely. The portion which remained in the bottom of the distilling tube when the distillation was interrupted also consisted of unchanged α body, as proved by the melting point.

Similarly the β body was subjected to a distillation at 1 mm. pressure in a bath at 135°–140°. The substance vaporized and sublimed on the tube as in the case of the α body. The crystals from the bottom of the tube, which had not been distilled, melted at 71°–72°; and those from the cooling tube, which had been formed from the vapor, melted at 73°–74°. Both, when mixed with β body (m. p. 71°–72°), melted at 71°–74°, showing, as in the α body experiment, that vaporizing has no tendency to change one isomer into the other.

As was anticipated, whereas physical methods failed to convert either form into the other, the action of chlorine readily converts the α body into the more stable β stereoisomer, just as traces of hydrogen bromide effect a change of maleic to fumaric acid, and as hydrogen chloride frequently converts one stereoisomeric oxime into the other. It was found, again, that the transformation by chlorine is a reversible one, the more stable β form being obtained in chief quantity but a small amount of the α body being formed even from the purest β form.

Eleven hundredths gram pure α compound was kept in contact with carefully washed and dried chlorine at 94° for four minutes; the product was then cooled and freed from chlorine. It showed a melting point of 69°–70°, indicating a change from the original body. The mass, dissolved in little chloroform and treated with ligroin, gave a very slight precipitate, which was filtered and allowed to dry while the mother liquor evaporated. This precipitate melted high and probably was the hydrochloride of the imidoester. It contained no active chlorine. The crystals obtained from the mother liquor evaporation were plainly the β body, as shown by their crystal plate form; they melted at 75.5°. A mixture of these plates and β body (m. p. 74°) melted at 74°, and after solidifying, it again melted at 74°. So these crystals were beyond

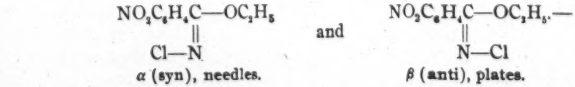
question the β form and proved that by the influence of chlorine the α stereoisomer can be converted into the β form.

As a parallel experiment the action of chlorine on pure β compound was studied to determine whether or not the action of chlorine on the α body is reversible. β crystals (m. p. 76°), whose absolute purity was established not only by their melting point but by the same process of fractionation used on them afterwards to extract the traces of α body formed by the action of chlorine, were heated with pure, dry chlorine at 95° for two minutes. The resulting mass was cooled and freed from chlorine. It was then extracted with a little cold ligroin, and the undissolved residue again subjected to treatment with chlorine and extracted with ligroin. This process was repeated until no more of the mass remained undissolved on treatment with ligroin. By evaporation, the solutions left crystals on the sides and bottoms of the beakers. The crystals on the bottom were obviously, from their form, β crystals, so the greatest attention was centered on the crystals on the sides, among which needle forms could be distinguished.

All the side crystals were collected and fractionated as usual from a chloroform solution hy precipitation with ligroin. A precipitate formed which melted at 97°–98°, and, mixed with pure α body, still melted at 98°–99°, but, when mixed with a little pure β body, the melting point was depressed to 70°–71°. These melting points prove absolutely that the above precipitate actually was the α form of the chlorimide.

Therefore we can finally say that the action of chlorine on the α and β forms is a reversible process and that in the rearrangement both isomers are formed, the β form in the larger quantity.

Stereoisomeric Forms of Ethyl Chlorimido-p-nitrobenzoate,



α (syn), needles. **β (anti), plates.**

The hydrochloride of ethyl imido-*p*-nitrobenzoate was prepared in the usual way from a chloroform solution of nitrobenzonitrile and 1.1 molecules of ethyl alcohol with the aid of hydrogen chloride.

The chlorimide was prepared, as in the other chlorimide preparations, by the action on the free ester, liberated from the salt by potassium bicarbonate, of hypochlorous acid. For each 3.42 grams of the hydrochloride the hypochlorous acid (2 molecules) formed from 2 grams of chlorine and 9 grams of sodium carbonate in solution as used. The chlorimide separates out easily, as a pure, white, granular precipitate. After being washed and dried, the precipitate was dissolved in chloroform, 3.5 cc. to each 1.0 gram of material, and four volumes of ligroin were added. The precipitate consisted of needles which melted at 95°–96°. The mother liquor gave crystals, principally needles, from the sides, melting at 72°–73°, and from the bottom of the beaker, melting at 88°–93°. Aside from the needles, only two or three very small plate or prism formed crystals appeared on the bottom of the beaker. These plates were carefully taken out and kept separately.

The above crystals (α body) melting at 95°–96° were analyzed and found to be pure ethyl chlorimido-*p*-nitrobenzoate.

0.0668 gram substance gave 0.0102 gram chlorine.

	Calculated for $C_9H_9N_2O_3Cl$.	Found.
Cl	15.50	15.35

It was evident that the needles were the predominant form and that the purest melted at 98°–99°, this being the highest melting point obtained for that form of crystals. They were called the α compound.

While both the precipitated chlorimide and the crystals obtained from the mother liquid were almost exclusively needle shaped, the appearance of the few tiny plates, mentioned above, gave some hopes of isolating a second form. So efforts were made to obtain a larger proportion of the plate form, if possible.

The first attempt was made by treating some of the needles at 95° with chlorine in the hopes of getting a transformation, since in both previous cases chlorine converted the needles almost completely into the more stable plate form. The treatment was continued for five minutes, then the resulting mass was dissolved in chloroform and an excess of ligroin added, throwing down a precipitate of needles, melting at 92°–94°. A few thick plates melting at 81°–85° were obtained from the mother liquid. These latter were also kept separate from the rest of the material. The plates obtained were so few that this method of securing more of the plate form was abandoned.

It was thought that the temperature at which the chlorination of the imidoester salt took place might have an effect on the yield of the plate form. A preparation was made at −5°, and another experiment was carried out at a temperature of 35°. Both preparations gave products similar to those obtained by chlorinating the imidoester at ordinary temperature. After precipitation of the high melting body from the chloroform solutions, the mother liquors, as usual, showed only a very few of the plate forms. Therefore these methods were discarded as a means for getting a larger yield of the plate form of the ethyl ester, and the method of picking out the plates, however few or tiny, whenever they appeared was resumed, and plate after plate collected.

Many times it was observed that crystal mixtures, either as precipitates or mother liquor crystals, which melted low, at 73°–81°, were persistently obtained even after many fractionations. Analyses of these low melting mixtures were made in order to determine whether the depression of the melting point was due to any foreign matter, or to the presence simply of the stereoisomer, which would not alter the analysis. So in each instance of a low melting body an analysis was made. As an example, one precipitate melting at 73°–83° was analyzed with the following result:

0.1185 gram substance gave 0.0183 gram chlorine.

	Calculated for $C_9H_9N_2O_2Cl$.	Found.
Cl	15.50	15.50

This and similar analyses of low melting mixtures proved them to be, in fact, mixtures of stereoisomeric ethyl chlorimido-*p*-nitrobenzoates, which were remarkably difficult to separate.

Low melting mixtures, as above, were dissolved in chloroform and precipitated by ligroin, and, as was expected, several good plates usually formed in the crystal mass left by the mother liquor evaporation. So by continued picking out of individual crystals of the plate form and by careful watching for products which melted low and analyzed well and using them for fractionation, 0.4 to 0.5 gram of the plate form material was finally obtained, as the result of six weeks' collecting.

This material was dissolved in the minimal amount of chloroform, and ligroin was added, giving a precipitate melting at 90°. Equal parts of this material and needles melting at 99°, when mixed, melted at 72°, proving conclusively that the plates or β form, whose highest melting point was observed at 90°, and the α body melting at 99° were two distinct compounds. An analysis of the β form resulted as follows:

0.0530 gram gave 0.0079 gram chlorine.

	Calculated for $C_9H_9O_3N_2Cl$.	Found.
Cl	15.50	14.96

Having shown that the two bodies were isomers and of the formula $C_9H_9O_3N_2Cl$, I next made experiments to prove the identity of their constitutions, exactly as in the case of the other chlorimides studied.

Some of the α form (m. p. 99°), dissolved in chloroform and ligroin, and treated with dry hydrogen chloride, gave a hydrochloride which, with water, formed ethyl *p*-nitrobenzoic ester, m. p. 57°.

The β form (m. p. 90°), treated in the same way, gave exactly the same result.

The chlorimidoesters have therefore exactly the same structure and must be stereoisomers, as in the previous cases.

To find out if the formation of the more unstable body

could be controlled, experiments were made on the effect of chlorine on each of the isomers. The α body (0.43 gram) was treated with chlorine at 100° for two minutes. The resulting product was dissolved in chloroform and precipitated with ligroin. The precipitate, somewhat gummy, melted at 82°–87°, and when mixed with pure β body the melting point dropped to 65°, proving that the precipitate was still the α form. The mother liquor gave crystals melting at 76°–78°, and mixed with the needle forms, m. p. 98°–99°, they melted at 80°–81°. So the mother liquor crystals were not the β form, and by the action of chlorine on the pure α body no decided transformation could be detected.

Some pure β plates, m. p. 90°, were treated with pure dry chlorine at 90°–100°. On cooling, the molten mass solidified quickly, showing that a high melting body was present, rather than a mixture. The mass, under a microscope, looked as if composed of needles only and gave, without further purification, a melting point of 93°. A mixture with pure plates caused the melting point to drop to 73°, again pointing to the presence of chiefly the needle form. Finally, some of the body in question was mixed with the pure α form (m. p. 98°–99°), and the mixture melted at 94°–95°, conclusively showing that the body was the α modification. This shows, then, that the β body is the more unstable, in this case, and is changed by the action of chlorine into the more stable form.

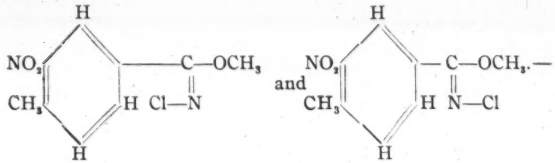
This fact, which is in direct contrast to the relative stability of the needle and plate forms of the methyl ester, and the undoubtedly closely related fact of the decided reversal in the proportions of the two stereoisomers formed by the action of hypochlorous acid on the imidoester, are of importance as giving us the chief means, as yet, of recognizing the actual space structure of the two isomers, as explained in the introduction (p. 155).

n-Propyl Chlorimido-p-nitrobenzoate, $p\text{-}NO_2C_6H_4C(:NCl)OC_3H_7$. —The imidoester hydrochloride was prepared from *p*-nitrobenzonitrile and 2 molecules of normal propyl alco-

hol in ether solution. The salt is a faintly yellowish, crystalline body, soluble in water.

From this salt the chlorimide was prepared, two molecules of hypochlorous acid being allowed to act on one molecule of the free base, liberated by potassium bicarbonate. The chlorimide proved to be a mobile oil, and all efforts to crystallize it failed.

Stereoisomeric Forms of Methyl Chlorimido-p-methyl-m-nitrobenzoate,



α (syn), plates. β (anti), needles.

m-Nitro-*p*-methylbenzonitrile was prepared by the action of nitric acid on paratolunitrile, 25 grams of the nitrile being added to a solution of 30 grams potassium nitrate in 500 cc. concentrated sulphuric acid. It was purified by distillation with steam and gave the melting point 99°; Leuckhart, who prepared it by the action of concentrated nitric acid on tolunitrile, gives the melting point as 100°.

The hydrochloride of methyl *m*-nitro-*p*-methylbenzoate was prepared from the nitrile and 1.1 molecules methyl alcohol in chloroform solution. For 10 grams of the nitrile, 40 cc. of chloroform were used to effect solution. The hydrochloride appeared as a white, crystalline body, soluble in water, giving the corresponding methyl ester, and changing to the amide by heat.

The salt was analyzed by a rapid titration with tenth normal sodium hydroxide, phenolphthalein being used as an indicator.[1] 0.4058 gram of the salt required 17.53 cc. of 0.1 N sodium hydroxide.

[1] Miss Barnard, of this labtoraory, has found that these imidoesters are such weak bases that they do not affect phenolphthalein and that their salts can therefore be titrated directly as containing the free acid. The titrations must be carried out rapidly and best from alkalinity to acidity, to avoid decomposition of the salt by water into an acid ester and ammonium chloride which holds the acid in neutral form.

	Calculated for $C_9H_{11}N_2O_5Cl$.	Found.
HCl	15.80	15.75

The free ester is obtained from an aqueous solution of the hydrochloride by potassium bicarbonate. It is a white, crystalline solid, melting at 60°–61°. It does not affect phenolphthalein, but does affect alizarin sulphonate, not strongly enough, however, for a quantitative determination of it by titration.

Methyl chlorimido-*m*-nitro-*p*-methylbenzoate was prepared from the free ester, liberated from its salt by potassium bicarbonate, with hypochlorous acid, two molecules being used. The crude product, which appeared semisolid and sticky, melted at 43°–44°. It was dissolved in chloroform, and, to separate any less soluble body, ligroin was added. A precipitate formed, which melted at 44°–46°; and crystals from the mother liquor melted also at 44°–46°, while some needles, formed near the bottom of the beaker, melted at 66°–67°. The precipitate, melting at 44°–46°, was analyzed and found to be reasonably pure, showing a chlorine content of 15.23 per cent. The calculated per cent is 15.51. So the precipitate in question was again dissolved in a minimal quantity of chloroform and four volumes of ligroin added. The resulting precipitate now melted at 82°–83°. The crystals from the first mother liquor and from this last one were fractionated again, but no further precipitate resulted. The crystals from the evaporated mother liquors were long, silky needles, mixed with an oily substance. Another fractionation failing to separate the needles from the oil, an analysis for chlorine was made. This gave a low result and showed that the low melting point of the mother liquor crystals in this case was not due to a mutual depression of melting points by two stereoisomers, but to the presence of some foreign substance. This was suspected to be unchanged free imido-ester, as the chlorination had been carried out at a temperature of 5° in order to insure the solidification of the material. The crude material was rechlorinated at room temperature and gave a solid which showed no tendency to liquefy; and

further preparations of the same body, made at room temperature, gave no further difficulty of this kind.

On further fractionation of this purer material, both plate and needle form crystals were observed. Several of the plates were taken out, crystallized, and found to melt at 83°–84°. The needle form crystals melted at 53°–60°. Two crystal forms of the chlorimide having presented themselves, efforts were now directed to getting more of the two distinct forms as pure as possible. Whenever plates appeared they were kept separate and then recrystallized. The needles, likewise, were carefully kept for purification, the crude product containing them chiefly melting at 60°–70°.

The plate material, 1.5 grams, was dissolved in 2.5 cc. chloroform and precipitated with 10 cc. of ligroin. The precipitate melted at 84°–85°, the highest point found for the plate form, which, as the higher melting variety, will be called the α form. To insure its purity, it was again dissolved and precipitated and showed the melting point unaltered, 84°–85°. These plates on analysis gave the following results:

0.0777 gram substance gave 0.0118 gram chlorine.

	Calculated for $C_9H_9O_3N_2Cl$.	Found.
Cl	15.51	15.29

This showed, then, that the plate form was pure.

The lower melting needle variety, or β form, 1.3 grams, was dissolved in 1 cc. chloroform and precipitated with 7 cc. ligroin. Then 0.5 cc. chloroform was added to partially dissolve the precipitate in the hope of getting it purer in this way. The precipitate was filtered and found to melt at 71°. The solution was again treated with ligroin and gave a second precipitate, melting at 70°. From another preparation the needles were dissolved in warm ligroin and allowed to crystallize from this solution. The needles last formed melted at 69°–70°. The highest melting point, then, for the pure needle form is 71°.

A mixture of equal parts of the body melting at 83°–84°

with that melting at 71° melted at 53°–54°, giving a depression characteristic of mixtures.

The needle form gave the following analysis:

0.1401 gram substance gave 0.0213 gram chlorine.

	Calculated for $C_9H_9N_2O_3Cl$.	Found.
Cl	15.51	15.23

The analyses having shown that both the needles and the plates had the empirical formula of the chlorimide of methyl 2-nitro-3-methylbenzoate, the identity of their constitution was proved as usual.

Some of the plates in ligroin, treated with dry hydrogen chloride and then with water, formed the methyl ester of 2-nitro-3-methylbenzoic acid, m. p. 47°–48°.

The needles, treated in the same way, gave the same result.

The effect of chlorine on each of the isomers was next studied. A small quantity of plates (m. p. 85°) was treated at 90° for two minutes with pure, dry chlorine. The resulting material melted at 63°–64°. It was dissolved in chloroform and the solution filtered and allowed to evaporate. Needle shaped crystals appeared, melting at 69°–70°. When the needles were mixed with pure plates, the melting point dropped to 54°–55°, showing that the needles were the β form, melting at 70°. It is obvious, then, that under treatment by chlorine the plate (α) form can be changed to the needle formed β body.

Then some of the needle form crystals were heated at 90° for five minutes with chlorine. The resulting substance melted at 64°–65°. It was then extracted with hot ligroin, which, when evaporated, left needles melting at 69°–70°, the melting point of the original crystals acted upon. So by the action of chlorine no appreciable conversion of the needle variety into the plate form is observed; the former is the more stable isomer.

Comparing the properties of this pair of stereoisomeric methyl esters with the stereoisomeric *methyl* chlorimidoesters of *m*- and *p*-nitrobenzoic acids, we note a peculiar contrast in properties; in the latter pairs, the plates repre-

sent the more *stable*, the more *soluble*, and the *lower melting* variety (β form); in the present series the more soluble and lower melting variety (β) is again the more stable one, but it crystallizes in the *needle* form. This contrast in crystal forms complicates the question of the determination of the configuration of the two forms by the method described in the introduction, but as all the properties, other than the crystal form, of the β variety of this pair agree with those of the β forms of the previously described methyl esters, we are inclined, for the present, to ascribe to the present β form, the needles, the same configuration (anti) as to the other β forms of methyl esters described, until further critical material for the determination of configurations can be obtained.

The molecular weights of the two stereoisomers were determined by the cryoscopic method, with benzene as the solvent.

(1) The β body (m. p. 72°), 16.815 grams solvent.

I. 0.2361 gram substance gave 0°.327 depression.[1]

II. 0.5961 gram substance gave 0°.810 depression.

	Calculated for $C_9H_9N_2O_2Cl$.	Found. I.	II.
Molec. Wt.	230.5	227.6	229.0

(2) The α form (m. p. 83°), 15.99 grams solvent.

I. 0.1538 gram substance gave $\left\{\begin{matrix} 0°.241[2] \\ 0°.216 \end{matrix}\right\}$ depression.

II. 0.3918 gram substance gave 0°.582 depression.

	Calculated for $C_9H_9N_2O_2Cl$.	Found. I.	II.
Molec. Wt.	230.5	236.0 and 211.4	223.1

It is shown, then, by the molecular weight determinations that the chlorimides in question have the formula $C_9H_9O_2N_2Cl$. They are, therefore, neither polymeric nor, as shown above, isomeric forms, the conclusion being confirmed that they are stereoisomers.

[1] The mean of two to four readings is given.

[2] The first reading, 0°.216, is rather far from the mean of other readings, averaging 0°.241; it is reported by itself, as there was reason to consider that the benzene absorbed a trace of moisture after the first reading.

Methyl Chlorimido-p-methylbenzoate,
p-$CH_3.C_6H_4C$ (:NCl)OCH_3, was prepared by chlorinating the corresponding imidoester with two molecules of hypochlorous acid.

The chlorimide appeared as a heavy, colorless oil which showed no signs of crystallizing, even when cooled. On standing two months in a vacuum desiccator it showed no trace of crystals. Under these conditions no attempt to purify the oil was made and it was analyzed in the crude condition.

The following results were obtained for chlorine content:

I. 0.1801 gram substance gave 0.0338 gram chlorine.
II. 0.1383 gram substance gave 0.0258 gram chlorine.

	Calculated for $C_9H_{10}NOCl$.	Found. I.	II.
Cl	19.31	18.79	18.71

Stereoisomeric Forms of Methyl Chlorimido-β-naphthoate,

β-$C_{10}H_7C(Cl{-}N){=}OCH_3$ and β-$C_{10}H_7{-}C(N{-}Cl){=}OCH_3$.—

This pair of chlorimides was prepared by chlorinating methyl β-naphthimidoester, obtained from its hydrochloride by potassium bicarbonate. As in previous experiments, the first step to separate possible isomers was made by dissolving the crude product in chloroform and adding ligroin. The precipitate appeared as a white, crystalline body melting at 123°, while from the mother liquor came crystals of a thin, plate form, melting at 66°–67°.

The precipitate, weighing 0.50 gram, was dissolved in 3 cc. of chloroform. From this solution 10 cc. of ligroin precipitated immediately a finely divided, crystalline body melting at 125°, which we will call the α body.

The crystals melting at 66°–67° were extracted with warm ligroin and this solution, on evaporating, left large, thin plates, melting sharply at 72°. This compound will be called the β form.

Recrystallization of each of the bodies melting at 125°

and 72° failed to change their melting points, so these are taken as the melting points of the α and β bodies.

The analyses gave the following results:

I. 0.0786 gram substance (α form) gave 0.0114 gram Cl.

II. 0.1765 gram substance (β form) gave 0.0282 gram Cl.

	Calculated for $C_{12}H_{10}NOCl$.	Found. I.	Found. II.
Cl	16.04	15.79	16.01.

These analyses show, then, that the composition of both bodies is $C_{12}H_{10}NOCl$.

To exclude the possibility of the two bodies being physical or crystal modifications, the melting points of the mixtures were taken. Equal parts of the two bodies melt at 66°; on solidifying and melting again, the mixture showed no change of melting point. A little of the β body with much of the α body melts at 67°; and little of the α form with much of the β body melted at 66°. A little of either, then, can perceptibly lower the melting point of the other.[1]

A quantity of the high melting α body was fused, allowed to cool, and crystallization started by rubbing it with a glass rod covered with a trace of powder of the β body. The solidified substance melted at 125°, showing that the α form maintains its own identity even when crystallizing in the presence of the β form. A similar experiment with the β body proved that it likewise maintains its own identity, m. p. 72°, when crystallizing in the presence of the solid α body. These experiments confirm the conclusion that these isomers can not be mere crystal modifications. The identity of the constitution of the two bodies was also found. Some of the α form, dissolved in ligroin and treated with dry hydrogen chloride, gave an imidoester hydrochloride, from which methyl β-naphthoate, melting at 77°, was obtained. Some synthetically prepared

[1] The peculiar nature of the depression suggests a closer and quantitative study of the question in this case and that of the ethyl ester, discussed by Dr. Hilpert. It appears possible that the methyl ester (m.p. 72°) is still a solid solution of a *pure* β form and the α form (m.p. 125°). This would account for the particularly large difference in melting points and the small depression of the melting point of the β form. The existence of stereoisomers is not made doubtful thereby, as explained under the ethyl ester.—J. Stieglitz.

ester melted at 76° and, when mixed with the above body, still melted at 76°–77°, showing that they are identical.

A parallel experiment to determine the structure of the β body showed that the corresponding product obtained from water melted at 77° and, when mixed with the body obtained similarly in the above experiment, again melted at 77°; mixed with the synthetic body, it melted at 76°–77°. So, beyond any doubt, both the α and β forms have the same constitution.

Molecular weight determinations were also made of the α and β bodies:

(1) The α body (m. p. 125°), 15.19 grams benzene as solvent.
I. 0.1428 gram substance gave 0°.224 depression.
II. 0.3234 gram substance gave 0°.511 depression.

	Calculated for $C_{12}N_{10}NOCl$.	Found	
		I.	II.
Molec. Wt.	219.5	222.5	220.9

(2) The β body (m. p. 72°), 18.87 grams solvent.
I. 0.2242 gram substance gave 0°.290 depression.
II. 0.3234 gram substance gave 0°.450 depression.

	Calculated for $C_{12}H_{10}NOCl$.	Found.	
		I.	II.
Molec. Wt.	219.5	217.0	202.0

In this case the molecular weight determinations bear great weight on account of the great difference in the melting points of the isomers. In no other case studied was there such a great difference in the melting points of two stereoisomers, but the molecular weight determinations set aside all doubt as to the bodies being anything but stereoisomers.

The Reversible Transformation of the Stereoisomers.—The attempt to transform one stereoisomer into the other by the action of chlorine, which had proved uniformly successful with all the pairs of stereoisomers hitherto described, led to the formation of gummy products in the case of the two methyl chlorimidonaphthoates. Such products were obtained by the action of chlorine at 115° on the α body and at 75° on the β form, as well as by the action of chlorine in carbon tetrachloride solution, in the cold, on both bodies. Fractionation with

ligroin did not separate any crystals from the mass, and as both stereoisomers crystallize remarkably well it was evident that other products were formed. The well-known fact that certain naphthalene derivatives form addition products very readily with the halogens points to the absorption of chlorine by the ring carbon atoms as the explanation of the action of chlorine. The nature of the gummy products was not further studied.

The transformation desired was accomplished accidentally and a new method of causing such transformations was discovered as the sequel of a test of the stability of the stereoisomers toward heat, with the object of ascertaining whether in the naphthalene series a "Beckmann rearrangement" would occur more easily than in the benzene series.[1]

The α body was heated to 150°–160° for two minutes. No escape of gas was noticed. After cooling, a sample was taken and found to melt at 115°–117°. The substance was again heated to 188°–190°; this time a slight, sharp odor was perceptible. The resulting material was active toward potassium iodide and acid. To determine whether, by a Beckmann rearrangement, any naphthylisocyanate at all was formed, I heated the product with water for five minutes to convert the isocyanate, if present, into dinaphthylurea. The solutions and solids remaining were extracted with ether, the ether readily dissolving all the solids. The ether, on evaporation, left a crystalline mass melting between 66° and 106°, which was very active in liberating iodine in an acidified iodide solution. This fact and the melting point raised the suspicion that a mixture of the two stereoisomers was present.

By the usual method of fractionation, a fraction was obtained whose melting point indicated unchanged α crystals. A second, more soluble fraction gave crystals melting at 66°, which, mixed with β crystals, melted at 66°–67°. This showed that from the high melting α modification, some of the lower melting β form had actually been formed. No dinaphthylcarbamide was found.

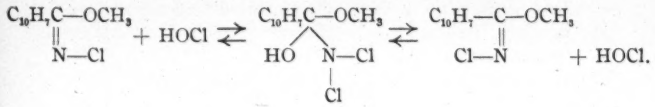
[1] Stieglitz and Earle: *Loc. cit.*

In a like manner, a quantity of the β modification (m. p. 72°) was heated at 180°–190° for two minutes, a sharp odor being given off. The resulting material was boiled with water and extracted with ether. The residue, left by the evaporation of the ether, melted at 105°–107°. This was fractionated by dissolving in very little chloroform, and the addition of ligroin produced a precipitate which melted at 112°–113°, and, when mixed with the pure α body, at 117°–120°. This melting point proves that some of the β body had been transformed into the higher melting α compound. Crystals from the mother liquor melted at 68°, and, mixed with the β body, at 68°–70°. Therefore a mixture of both the α and β modifications was formed.

To find out just what had caused the transformation, whether the high temperature, the boiling with water, or merely the evaporation in ether solution, a small quantity, 0.10 gram, of the β body was dissolved in ether and the solution allowed to evaporate. The resulting crystals melted at 72°, just as before the treatment; therefore solution in ether causes no transformation, and the bodies are not mere physical isomers. The recovered crystals were boiled a moment with water and heated half an hour on the steam bath. The mixture was then extracted with ether and the crystals resulting from its evaporation were fractionated from 0.5 cc. chloroform and 3–4 cc. of ligroin. The precipitate which formed melted at 96° and, mixed with the α form, at 107°, showing that some change into the α form had taken place. The mother liquor from the precipitate left small, white plates melting at 71°, showing that the remaining substance was the unchanged β body.

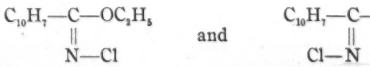
Similarly, a control experiment was made on the α body, a small quantity of which was treated with water. The ether extract of the resulting mixture left crystals, which, on fractionating, gave a precipitate melting at 121°. The first crystals from the mother liquor melted at 95°; others, on the sides of the beaker, melted at 65°–67°; and the last, mixed with the β body (m. p. 71°), melted at 66°–70°; proving conclusively that some of the β modification was present.

These experiments showed, first, that the two stereoisomers can be transformed one into the other by a reversible process, a mixture of the two resulting either from the pure α or the pure β body; and second, that the transformation is caused essentially by heating with water. Since dry heat alone has no such effect, it is practically certain that the transformation is produced by the action of a trace of hypochlorous acid or chlorine produced by the action of water on the chlorimidoester, this trace acting, then, as did the chlorine in all the previous transformation experiments, probably through the intermediate formation of an addition product:



The transformation is considered particularly important on account of the great difference in the melting points of the two stereoisomers.

The Stereoisomeric Forms of Ethyl Chlorimido-β-naphthoate,



Slosson,[1] working in this laboratory, prepared ethyl chlorimido-β-naphthoate by the action of bleaching powder on ethyl imido-β-naphthoate, and described it as a well crystallizing substance of melting point 71°, *forming needles and plates* by crystallization from warm ligroin. With the object of getting these needles and plates and separating them, mechanically, if need be, I prepared the body from chloride of lime solution, exactly as described by Slosson, as well as several times by the use of hypochlorous acid prepared by the method described in these pages. Crystals melting at 64°–65° were readily obtained as the first fraction by the first crystallization of the crude product, and by further crystallization the substance of melting point 72° was obtained.

[1] Slosson: This Journal, **29**, 289 (1903).

The needles and plates, however, proved to be the same substance, of the same melting point. The plates were exceedingly thin lamellae and looked like needles at certain angles, and under the microscope no essential difference between the two forms could be noted. These, then, were not stereoisomeric forms. Nevertheless, the formation and presence of stereoisomers in the reaction product was established conclusively, as follows: from the action of hypochlorous acid on the free ethyl imido-β-naphthoate, a product results which, without fractionation, almost invariably melts as low as 36°–39°, and which nevertheless gives, on analysis, excellent figures for a pure ethyl chlorimido-β-naphthoate. For instance, in one case the following result was obtained for crystals melting at 39°:

0.1117 gram substance gave 0.0168 gram chlorine.

	Calculated for $C_{13}H_{12}NOCl$.	Found.
Cl	15.17	15.06

For further purification this product (3 grams) was extracted with 35 cc. of warm ligroin. The solution, on evaporating, left crystals melting at 64°–65° on the bottom of the beaker, and the last crystals to appear, on the sides, melted at 38°–48°. The first crystals (m. p. 64°–65°), after several fractionations, gave a product which melted constantly at 72°. This substance, which was described and analyzed by Slosson, will be called the α form, and is most likely the syn stereoisomer (see above[1]). The low melting crystals were all collected and extracted with ligroin and the solution allowed to evaporate. At first, on cooling, needles formed, which melted at 38°; and the crystals forming later on the sides of the beaker melted at 37°–39°. When about one half the liquor had evaporated, it was decanted and allowed to evaporate further in another beaker. After a time, tufts of needles appeared, which melted between 39° and 47°. The solution was again decanted and allowed to evaporate. More of the crystals melting between 39° and 48° appeared. An analysis of the latter crystals was made and yielded the following results:

[1] Page 156.

0.1198 gram substance gave 0.0179 gram Cl.

	Calculated for $C_{18}H_{12}NOCl$.	Found.
Cl	15.17	14.96

The crystals melting at 39°–48°, when mixed with an equal quantity of the body melting at 72°, melted *completely* at 39°–41°, showing a lowering of about 7° for part of the substance, which pointed to a difference in the two bodies.

The mixture of crystals melting at 38°–40° were repeatedly extracted with ligroin, and finally a product melting constantly at 39° was obtained. As will be shown presently, the substance of the low melting point (39°) has exactly the same structure as the compound melting at 72°; and the analyses given above, proving its purity beyond a doubt, show that *no foreign impurity* is the cause of the low melting point. The body melting at 39° must then unquestionably be either the second stereoisomeric (β) form itself or, more likely, a mixture of two stereoisomeric forms, one of which melts at 72°, while the second could not be completely separated from its stereoisomer, owing to the great solubility of the two forms, even in ligroin, saturated solutions of the two forms in each other giving the minimum melting point 39°. We are inclined to hold that the substance is not the pure β form, but rather a mixture, as described, of the α and β forms, and that the pure β compound melts at 48° or higher. The following facts lead us to this belief:

(1) The melting point of the fractions melting between 39° and 48° is depressed by the α form.

(2) The α form does not depress the melting point below 39°, as it would if the substance melting at 39° did not already contain the α body mixed with the β compound.

(3) The existence of a minimum melting point corresponds perfectly to the minimum melting points observed for the mixture of the two stereoisomers in every other series. The only difference between the behavior of this mixture and all the others lies in the impossibility of separating the two stereoisomers completely; but as the more insoluble α form was isolated and found to melt at 72°, there can be no question

that in the substance melting at 39° the second stereoisomer must be present. It may be recalled that the discovery of the stereoisomers of the chlorimide of methyl *m*-nitrobenzoate started from the same initial fact that a mixture, giving perfect analyses, melted 30° lower than the fractionated product, and that the second stereoisomer, whose presence was deduced from this behavior, was found in short order. For these reasons it is considered that the above behavior proves that ethylchlorimido-β-naphthoate also exists in two stereoisomeric forms.

The proof that the α and β forms have the same constitution was brought, as in the cases of the other stereoisomeric chlorimides, by converting the chlorimides into the hydrochloride of the imidoester and decomposing the salt by water into ammonium chloride and the ethyl ester of β-naphthoic acid, and by converting the salt into β-naphthylamide and ethyl chloride by heat.

The ethyl naphthoate obtained from the α body (m. p. 72°) and from the α, β mixture (m. p. 39°) melted at blood temperature, and mixtures of the two did likewise. This indicated that the ethyl group is attached to oxygen in these bodies, also that they both have the same structural formula. A second rigorous proof was obtained by heating the hydrochlorides of the imidoester, obtained by passing dry hydrogen chloride into a ligroin solution of the mixture melting at 39° and also of the α body. Both hydrochlorides decomposed at 135°, leaving residues melting sharply at 191°–192°, the melting point of β-naphthamide. A mixture of equal parts of the β-naphthamide (m. p. 191°–192°) formed from the α body and that formed from the α, β mixture melted also at 191°–192°. This, then, proves unquestionably that in this chlorimide, both in the α body (m. p. 72°) and in the α, β mixture (m. p. 39°), we have compounds of the same structure and composition.

Since, then the two bodies have different melting points and analyze as pure $C_{13}H_{12}NOCl$, and both have the same structure, we must have two stereoisomers.

The ethyl chlorimidonaphthoate is the last chlorimidoester

examined for which I have been able to establish the existence of a pair of stereoisomeric esters. Some experiments with two other chlorimidoesters and two bromimidoesters, which in spite of the scrupulous application of the same methods of preparation, fractionation, and transformation, gave negative results, are of peculiar interest as showing the difficulties attending the formation of such isomers. In view of the formation of the stable variety in considerable excess, in all the above cases, and of the transforming effect of chlorine and, undoubtedly, also of hypochlorous acid, and, finally, in consideration of the sharp and characteristic indications of the occurrence of stereoismerism, as shown in the study of melting points, which makes it comparatively easy now to recognize its occurrence, we are led to conclude that the failure to obtain stereoisomers is probably due less to difficulties in separating any stereoisomers than to the fact that the stable form must be favored to such an extent in the preparation that the unstable one is scarcely present, if at all. A failure to establish the existence of stereoisomers for a solid chlorimidoester is limited to two cases. More important and interesting is the fact that all endeavors to prepare stereoisomeric bromimidoesters have thus far been unsuccessful, the last attempt having been made with methyl β-naphthoate, for which the corresponding chlorimide stereoisomers melt 50° apart.[1] The theoretical significance of these facts having been discussed in the introduction, the experimental results for these compounds will be briefly given.

Methyl Chlorimido-p-brombenzoate, p-$BrC_6H_4C(:NCl)OCH_3$.[2] —This chlorimide was prepared by chlorinating the corresponding imidoester with two molecules of hypochlorus acid. The chlorimide appeared at first as an oil, which solidified only on freezing.

The solid, oily mass was dissolved in warm ligroin, and when the solution cooled, a precipitate settled out. This

[1] See note, p. 179

[2] The imidoester was obtained from p-brombenzonitrile, which was prepared from p-brombenzoic acid (Kahlbaum's preparation) by the successive treatment with phosphorus pentachloride, ammonia, and phosphorus pentoxide.

precipitate melted at 57°.5, and the crystals from the mother liquor, branches of needles, melted at 54°–55°.

More of the crude chlorimide, dissolved in chloroform, failed to give a precipitate on the addition of ligroin. This solution, on evaporating, gave crystals which were rubbed up with cold ligroin to take out the more soluble portion, and filtered. These crystals melted at 58°–59°, and the crystals from the mother liquor, plates, melted at 60°.

The plates melting at 60°, mixed with the body melting at 58°–59°, melted at 58°–59°, and when mixed with the needles melting at 55°, at 56°–57°. The plates and needles, therefore, cannot be considered as representing stereoisomeric substances, but rather two crystal or physical modifications of a single substance, as no depression of the melting point occurs when they are mixed. Such a case is not uncommon with the chlorimidoesters, as will be discussed more fully in connection with the next compound studied, and it shows how the presence of stereoisomers may be simulated by crystal modifications. The analysis of the body showed it to be pure.

0.0518 gram substance gave 0.0073 gram chlorine.

	Calculated for $C_8H_7NOClBr$.	Found.
Cl	14.26	14.26

Methyl Chlorimido-m-nitro-p-brombenzoate, p-Br-m-$(NO_2)C_6H_3C$: $(NCl)OCH_3$. Although the investigation of the chlorimide prepared from methyl imido-p-brom-m-nitrobenzoate[1] did not lead to the isolation of a further pair of stereoisomers, it proved particularly instructive as emphasizing the difference in behavior of two crystal forms of a single substance and of two stereoisomers in the critical tests used. The new chlorimide was observed to occur in two modifications, crystallizing sometimes as needles, sometimes as plates, just like some of the stereoisomers previously described. Low melting fractions were also very frequently obtained. But the following vital differences in behavior, in the present case, were observed: (1) the low melting frac-

[1] The hydrochloride of the imidoester was obtained in the usual way from m-nitro-p-brombenzonitrile. The nitrile was obtained from p-brombenzonitrile by Schöpff's method (Ber. d. chem. Ges., **23**, 3439 (1890)).

tions invariably gave quite low results when analyzed for active chlorine, which showed that the depression of the melting point could have been largely, or altogether, due to some foreign substance (probably some nonchlorinated imidoester); (2) the melting points of these low melting fractions were invariably raised by admixture of the pure chlorimide; (3) no depression of the melting point is observed when the melting point of a mixture of needles and plates is taken; (4) one and the same material, on recrystallization, was obtained sometimes in the form of needles, sometimes as massive plates, according to the method of crystallization. This is the behavior of physical modifications of a substance, and, by contrast to the fundamentally different behavior of the stereoisomers isolated, confirms our conclusions regarding the latter.

The following statement of a part of the experimental results obtained will be sufficient to serve as a foundation for the above parallel. A light yellow solid resulted when methyl imidobromnitrobenzoate was treated with hypochlorous acid. The crude product, 3 grams, was dissolved in 6 cc. chloroform, and on the addition of 21 cc. ligroin a precipitate was thrown down, melting at 89°–90°. From the mother liquor needles melting at 56°–63° and plates melting at 89°–90° were obtained. The precipitate and plates melting at 89°–90° gave the same melting point when mixed. The two were dissolved together in 3.5 cc. chloroform and 20 cc. ligroin were added, producing a precipitate of *needles* melting at 95°, while plates (m. p. 90°) were obtained from the mother liquor. The needles and plates, mixed, melted at 92°–93°. The needles (m. p. 95°) were analyzed with the following result:

0.0946 gram substance gave 0.019 gram chlorine.

	Calculated for $C_8H_6N_2O_4ClBr$.	Found.
Cl	12.07	11.80

Both needles and plates were obtained showing low melting points ranging between 59° and 90°, and in either case the melting point was raised by the admixture of pure substance, m. p. 94°–95°. An analysis of such low melting needles (59°–66°) gave a chlorine content of 11.37 per cent (calculated

12.07). It is obvious from these facts that we would not be justified in considering the plates and needles as representing stereoisomeric forms in this case. This conclusion, nevertheless, does not of course, exclude the possibility of two stereoisomers existing, it will be recalled that one of the first pair of stereoisomers discussed, the α form of methyl chlorimido-*m*-nitrobenzoate, crystallizes in two forms, usually forming silky needles, but yielding rectangular plates by slow evaporation of its solutions, both these forms being entirely different from the third form, the stereoisomeric β body[1]. But, in the present case, we simply have one of the many well-known instances of the formation of a stable stereoisomer in such preponderance that the less stable form is either not produced at all or in such slight amount that it becomes exceedingly difficult to isolate it. As was to be expected, the action of chlorine on our product (m. p. 94°–95°) proved it to be the stable form, most of the body being recovered unchanged. A small fraction was obtained melting between 66°–79°, and as only pure chlorimide was used, it may very well be that a small amount of a less stable stereoisomer was formed, as was rigorously proved in previous cases; but the material was insufficient for any present attempt to isolate the missing stereoisomer.

Methyl Chlorimido-p-anisate, p-CH_3O-$C_6H_4C(:NCl)OCH_3$.—The hydrochloride of methyl imidoanisate was prepared from anisonitrile, which was readily obtained from the acid, by way of the chloride and the amide.

0.2772 gram of substance gave 0.0500 gram HCl.

	Calculated for $C_9H_{11}NO_2Cl$.	Found.
HCl	18.08	18.07

The anisic imidoester was then liberated by potassium bicarbonate and chlorinated with two molecules of hypochlorous acid. The product was a faintly yellow oil, with a sharp odor. All efforts to crystallize it by cooling or other mechanical means failed. The oil was analyzed as follows:

0.2526 gram substance gave 0.0448 gram Cl.

	Calculated for $C_9H_{10}NO_2Cl$.	Found.
Cl	17.76	17.66

[1] Stieglitz and Earle: *Loc. cit.*, p. 403.

Methyl Bromimido-m-nitrobenzoate, *m*-$NO_2C_6H_4C(:NBr)OCH_3$. —The first attempts to prepare a pair of stereoisomeric bromimidoesters were made with methyl imido-*m*-nitrobenzoate, from which Stieglitz and Earle had obtained the first pair of chlorimidoesters. Hypobromous acid was used as the reagent. It was obtained by the action of bromine on sodium hydroxide, the latter usually in slight excess beyond that required by the formulation

$$2NaOH + Br_2 \longrightarrow NaOBr + NaBr + H_2O.$$

The action with the imidoester hydrochloride is as follows:

$$NaOBr + NO_2C_6H_4C(NH_2Cl)OCH_3 \longrightarrow NaCl + H_2O + NO_2C_6H_4C(NBr)OCH_3.$$

A large excess of alkali reverses this action, giving a very impure product; less alkali was not used because of the transforming power of the free halogen. But a considerable excess of hypobromite was occasionally used with the object of hastening the action by mass action, so as to separate as quickly as possibly any unstable, solid bromide which might be formed. Several preparations were made in which the hypobromite was varied from one to eight molecules. The former gave yellowish precipitates of low melting points (*e. g.*, 37°) and even oils, but they were very impure, as shown by analysis, and little could be done with these products, which unquestionably contained unchanged free imidoester. The large excess (8 molecules) of hypobromite gave at once a good yield of flocculent precipitate, only slightly colored. It was dried and dissolved in ligroin, and the solution allowed to evaporate. There appeared, after a time, large plates melting at 95°. There were also needles, in one case, melting at 83°, and, in another, at 91°. These two apparently different forms gave a little hope of finding stereoisomers. More of the bromimide was then prepared as above, and again extracted with ligroin and then chloroform. On letting the ligroin evaporate till crystals appeared and decanting the supernatant liquor, several fractions were obtained. In the first fraction, plates melting at 97°–98°, along with needles

melting at 86°–87°, were found. These latter, mixed with equal parts of the plates, still melted at 86°, showing them to be, most likely, different crystal forms of the same body.

Another method of purifying the crude bromimide was to dissolve the substance in acetone and precipitate it with water.

From several ligroin extracts both needles and plates were obtained, and when the needles were again recrystallized from ligroin and chloroform, besides needles, some plates appeared when nearly all the solution was evaporated. The needles are seen under a microscope *to have the same end angles* as the plates. The recrystallized needles melted at 101°. After recrystallizing the needles once more it was found that their melting point remained constant. The analysis of the body melting at 101°, of which very little was obtained, resulted as follows:

0.0074 gram substance gave 0.0049 gram bromine.

	Calculated for $C_8H_7N_2O_3Br$.	Found.
Br	30.88	30.43

The plate form crystals were also recrystallized from ligroin and chloroform. On evaporation of the solution, both needles and plates remained, the needles melting at 97° and the plates at 91°. The plates, after being pulverized and leached with ligroin, melted at 96°. Then they were recrystallized from ligroin once more and gave the melting point 99°.9.

A mixture of the plates (99°.5) and the needles (101°) melted at 99°–100°, showing identity and therefore absence of stereoisomers.

From these experiments it was concluded that the needles and plates obtained are not stereoisomeric forms, as in the case of the chlorimides. They have the *appearance* of crystal varieties, but lack the criteria of stereoisomeric forms: needles are obtained from ligroin solutions and plates are formed when chloroform is present, due, probably, to the slower evaporation; both forms appear under the microscope to have the *same crystalline structure*. The most critical test

of all, the fact that there was no characteristic depression of melting points when a mixture of plates and needles was used, emphasizes the total differences in the behavior of the chlorimides and the bromide.

In order not to overlook the possibility that the bromimide formed might be the unstable modification, although this was scarcely likely, a small amount of the bromimide was heated in a tube to 100° for one half hour in the presence of bromine vapors. In a second similar experiment the bromimide was kept at 100° for *two* minutes; in another, at 95° for two minutes; and in a final one, at 120° for one minute; all gave the original bromimide. Therefore it can be stated that as far as the above experiments go, no stereoisomers of methyl bromimido-*m*-nitrobenzoate were found.

Half a year later, still other experiments were made, the method being employed which was used most successfully in preparing stereoisomeric chlorimides, *viz.*, the use of hypobromous acid made from bromine and sodium carbonate or bromine and a suspension of mercuric oxide in water. The free ester was liberated from its salt by potassium bicarbonate and borax and treated with the hypobromous acid, prepared as above. The bromimide always appeared as a solid and gave good yields of a product of a high degree of purity, but, as in the initial experiments, no stereoisomers could be isolated; in fact, identity was proved, just as before, by the melting points.

The following are analyses of several preparations of the methyl *m*-nitro-bromimidoester:

I. 0.1135 gram substance gave 0.0346 gram Br.
II. 0.0734 gram substance gave 0.0227 gram Br.
III. 0.1550 gram substance gave 0.0475 gram Br.
IV. 0.1947 gram substance gave 0.0603 gram Br.

	Calculated for $C_8H_7O_3N_2Br$.	Found.			
		I.	II.	III.	IV.
Br	30.89	30.49	30.92	30.65	30.96.

Methyl Bromimido-β-naphthoate, β-$C_{10}H_7C(:NBr)OCH_3$.

Because of the very great difference in the melting points and solubility of the stereoisomeric methyl chlorimidonaph-

thoates, it was thought that if stereoisomeric methyl bromimidonaphthoates existed, they would also probably be widely different as to solubility and melting points, and so be easily isolated.

The bromimide was prepared from the hydrochloride of methyl imidonaphthoate by treatment with hypobromous acid, the free ester being liberated by potassium bicarbonate.

The product was a light yellow, granular precipitate, melting at 98°–99°. Three grams were dissolved in 10 cc. of chloroform and then 40 cc. of ligroin were added, giving a crystalline precipitate melting at 99°–100°. The mother liquor gave crystals on the sides and bottoms of three beakers, melting practically at the same temperature, 97°–98°, 96°–97°, and 95°. Each, when mixed with the higher melting body, melted unchanged or higher, showing that all the different products were identical and that no stereoisomers were present.

An attempt was made to transform the bromimide by means of hot water, but the substance was decomposed, one of the products of decomposition being β-naphthamide.

The introductory statement contains a complete summary of the results and conclusions reached, and reference is made to it at this place.

In conclusion, I wish to take this opportunity to express my gratitude to Professor Stieglitz for his careful supervision of this work and for his personal inspiration.

CHICAGO, September, 1907.

THE OSMOTIC PRESSURE OF CANE SUGAR SOLUTIONS AT 15°.[1]

BY H. N. MORSE AND B. MEARS.

The measurements of the osmotic pressure of cane sugar solutions at 15°, like those of cane sugar at 10°,[2] and of glu-

[1] The work upon osmotic pressure which is in progress in this laboratory is aided by grants from the Carnegie Institution. The earlier papers upon the subject will be found in THIS JOURNAL, **26**, 80; **28**, 1; **29**, 173; **32**, 93; **34**, 1; **36**, 1 and 39; **37**, 324, 425, and 558; **38**, 175; **39**, 667; **40**, 1.

[2] THIS JOURNAL, **39**, 667.

cose at the same temperature,[1] are characterized by the minuteness of the loss in rotation which the solutions suffered while in the cells, and likewise by the constancy of the temperature which was maintained in the bath. The bearing of these factors upon the accuracy of the results has been so often discussed in these papers that it is necessary now only to recall the fact—which cannot be too strongly emphasized—that the principal obstacles to the exact measurement of osmotic pressure are "*thermometer effects*," and the *dilution of the cell contents* under conditions which make it impossible to determine whether, and to what extent, such dilution *preceded* or *followed* the measurement. With reasonable skill and patience, all other known sources of error can be brought under fairly good control, but the suppression of these has cost us several years of continuous effort. The beneficial result of this elimination of the largest and most obstinate sources of uncertainty will be seen in the latter part of this paper, where it is shown that the osmotic pressure of cane sugar solutions has a decided temperature coefficient, a fact which could not be established while the possible experimental errors were still large.

The customary duplicate determinations of ten concentrations of solution, ranging from 0.1 to 1.0 weight normal, have been made, and the results of the individual experiments are given in Tables I. to XX. In the tables which follow (XXI. and XXII.), these are summarized in the usual ways:

[1] This Journal, **40**, 1.

Table I.

0.1 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 12°.7; (2) at conclusion of expr., 12°.7; loss, 0. *Manometer:* No. 9; volume of nitrogen, 433.07; displacement, 0.05 mm. Cell used, G. Resistance of membrane, 535,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.43; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 1.96. Time of setting up cell, 3.00 P.M., Apr. 9, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Apr. 11.						
3.30 P.M.	15°.0	15°.0	143.77	2.47	2.35	0.12
Apr. 12.						
9.00 A.M.	15°.0	14°.8	143.25	2.46	2.35	0.11
				2.47	2.35	0.12

Molecular osmotic pressure, 24.65.
Molecular gas pressure, 23.50.
Ratio of osmotic to gas pressure, 1.049.

Table II.

0.1 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 12°.7; (2) at conclusion of expr., 12°.7; loss, 0. *Manometer:* No. 5; volume of nitrogen, 471.94; displacement, 0.01 mm. Cell used, A_3. Resistance of membrane, 28,421. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.45; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 2.13. Time of setting up cell, 4.00 P.M., Apr. 28, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Apr. 29.						
10.00 P.M.	15°.0	15°.6	158.29	(2.46)	2.35	....
Apr. 30.						
8.30 A.M.	15°.0	15°.8	157.27	2.48	2.35	0.13
12.30 P.M.	15°.0	15°.4	157.61	2.48	2.35	0.13
2.30 P.M.	15°.0	15°.6	157.37	2.49	2.35	0.14
				2.48	2.35	0.13

Molecular osmotic pressure, 24.83.
Molecular gas pressure, 23.50.
Ratio of osmotic to gas pressure, 1.056.

Table III.

0.2 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 24°.9; (2) at conclusion of expr., 24°.8; loss, 0°.1 = 0.4 per cent. *Manometer:* No. 11; volume of nitrogen, 465.94; displacement, 0.01 mm. Cell used, G. Resistance of membrane, 220,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.48; (3) dilution, 0.01; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 4.19. Time of setting up cell, 4.00 P.M., May 7, 1907.

	Temperature.		Volume N_2.	Pressure.		
Time.	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 7.						
11.00 P.M.	14°.8	15°.0	86.11	4.90	4.70	0.20
May 8.						
12.30 P.M.	15°.1	15°.8	85.85	4.92	4.70	0.22
4.00 P.M.	14°.8	15°.3	85.85	4.92	4.70	0.22
May 9.						
12.00 M.	14°.9	15°.2	86.06	4.90	4.70	0.20
				4.91	4.70	0.21

Molecular osmotic pressure, 24.55.
Molecular gas pressure, 23.50.
Ratio of osmotic to gas pressure, 1.044.

Table IV.

0.2 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 25°.0; (2) at conclusion of expr., 25°.0; loss, 0. *Manometer:* No. 24; volume of nitrogen, 472.58; displacement, 0.06 mm. Cell used, B_3. Resistance of membrane, 377,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.54; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 4.26. Time of setting up cell, 12.00 M., May 3, 1908.

	Temperature.		Volume N_2.	Pressure.		
Time.	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 4.						
8.30 A.M.	15°.0	15°.0	88.66	4.89	4.70	0.19
12.30 P.M.	15°.0	14°.9	88.63	4.89	4.70	0.19
10.00 P.M.	15°.0	15°.0	88.34	4.91	4.70	0.21
May 5.						
8.30 A.M.	15°.0	15°.0	88.64	4.89	4.70	0.19
				4.90	4.70	0.20

Molecular osmotic pressure, 24.50.
Molecular gas pressure, 23.50.
Ratio of osmotic to gas pressure, 1.043.

Table V.

0.3 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 36°.6; (2) at conclusion of expr., 36°.6; loss, 0. *Manometer:* No. 21; volume of nitrogen, 477.75; displacement, 0.28 mm. Cell used, B. Resistance of membrane, 367,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.50; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 5.9. Time of setting up cell, 12.30 P.M., May 11, 1907.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
May 11.						
8.00 P.M.	15°.1	16°.6	61.29	7.32	7.05	0.27
May 12.						
12.00 M.	15°.1	15°.1	61.43	7.30	7.05	0.25
May 13.						
9.00 A.M.	15°.0	15°.2	61.31	7.30	7.05	0.25
				7.31	7.05	0.26

Molecular osmotic pressure, 24.37.
Molecular gas pressure, 23.50.
Ratio of osmotic to gas pressure, 1.037.

Table VI.

0.3 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 36°.7; (2) at conclusion of expr., 36°.7; loss, 0. *Manometer:* No. 5; volume of nitrogen, 471.94; displacement, 0.04 mm. Cell used, B_3. Resistance of membrane, 224,000. *Corrections:* (1) atmospheric pressure, 0.98; (2) liquids in manometer, 0.59; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 5.6. Time of setting up cell, 5.00 P.M., May 8, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
May 9.						
8.30 A.M.	15°.0	15°.0	60.97	7.37	7.05	0.32
May 10.						
1.00 A.M.	15°.0	15°.1	61.18	7.34	7.05	0.29
11.00 P.M.	15°.0	15°.2	61.10	7.34	7.05	0.29
				7.35	7.05	0.30

Molecular osmotic pressure, 24.50.
Molecular gas pressure, 23.50.
Ratio of osmotic to gas pressure, 1.043.

Table VII.

0.4 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 47.9; (2) at conclusion of expr., 47°.9; loss, 0. *Manometer:* No. 13; volume of nitrogen, 438.84; displacement, 0.02 mm. Cell used, B_3. Resistance of membrane, 560,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.17. Time of setting up cell, 4.00 P.M., May 16, 1908.

Time.	Temperature. Solution.	Temperature. Manometer.	Volume N_2.	Pressure. Osmotic.	Pressure. Gas.	Pressure. Difference.
May 17.						
12.00 M.	15°.0	15°.8	42.70	9.77	9.40	0.37
4.00 P.M.	15°.1	15°.6	42.63	9.78	9.40	0.38
11.00 P.M.	15°.0	15°.8	42.70	9.77	9.40	0.37
May 18.						
4.30 A.M.	15°.0	15°.8	42.67	9.77	9.40	0.37
				9.77	9.40	0.37

Molecular osmotic pressure, 24.43.
Molecular gas pressure, 23.50.
Ratio of osmotic to gas pressure, 1.039.

Table VIII.

0.4 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 47°.9; (2) at conclusion of expr., 47°.9; loss, 0. *Manometer:* No. 5; volume of nitrogen, 471.94; displacement, 0. Cell used, A_3. Resistance of membrane, 70,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.89. Time of setting up cell, 4.00 P.M., May 16, 1908.

Time.	Temperature. Solution.	Temperature. Manometer.	Volume N_2.	Pressure. Osmotic.	Pressure. Gas.	Pressure. Difference.
May 17.						
7.00 A.M.	15°.1	15°.8	46.53	9.77	9.40	0.37
12.00 M.	15°.0	15°.8	46.51	9.78	9.40	0.38
11.00 P.M.	15°.0	15°.8	46.52	9.77	9.40	0.37
May 18.						
4.30 A.M.	15°.0	15°.8	46.48	9.78	9.40	0.38
				9.78	9.40	0.38

Molecular osmotic pressure, 24.45.
Molecular gas pressure, 23.50.
Ratio of osmotic to gas pressure, 1.040.

Table IX.

0.5 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 58°.7; (2) at conclusion of expr., 58°.7; loss, 0. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.51 mm. Cell used, A_3. Resistance of membrane, 26,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 10.47. Time of setting up cell, 4.00 P.M., Apr. 21, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2	Osmotic.	Gas.	Difference.
Apr. 21.						
11.00 P.M.	15°.0	15°.3	32.06	(12.27)	11.75	(0.52)
Apr. 22.						
9.00 A.M.	15°.0	15°.1	32.03	12.29	11.75	0.54
12.00 M.	15°.0	15°.2	32.04	12.28	11.75	0.53
3.00 P.M.	15°.0	15°.4	31.99	12.30	11.75	0.55
				12.29	11.75	0.54

Molecular osmotic pressure, 24.58.
Molecular gas pressure, 23.50.
Ratio of osmotic to gas pressure, 1.046.

Table X.

0.5 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 58°.7; (2) at conclusion of expr., 58°.7; loss, 0. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.09 mm. Cell used, B_3. Resistance of membrane, 122,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 10.19. Time of setting up cell, 4.30 P.M., May 12, 1908.

	Temperature.		Volume.	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
May 13.						
8.30 A.M.	15°.0	16°.0	32.07	12.27	11.75	0.52
May 14.						
8.30 A.M.	15°.1	16°.1	31.99	12.30	11.75	0.55
3.00 P.M.	15°.1	16°.3	32.02	12.29	11.75	0.54
				12.29	11.75	0.54

Molecular osmotic pressure, 24.58.
Molecular gas pressure, 23.50.
Ratio of osmotic to gas pressure, 1.046.

Table XI.

0.6 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 69°.1; (2) at conclusion of expr., 69°.1; loss, 0. *Manometer:* No. 21; volume of nitrogen, 362.46; displacement, 0.18 mm. Cell used, G. Resistance of membrane, 121,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.50; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 9.70. Time of setting up cell, 4.30 P.M., Apr. 22, 1908.

Time.	Temperature. Solution.	Manometer.	Volume N_2.	Pressure. Osmotic.	Gas.	Difference.
Apr. 23.						
4.30 P.M.	15°.0	15°.6	23.56	14.91	14.09	0.82
9.30 "	15°.0	15°.4	23.57	14.91	14.09	0.82
Apr. 24.						
8.30 A.M.	15°.0	15°.4	23.59	14.90	14.09	0.81
				14.91	14.09	0.82

Molecular osmotic pressure, 24.85.
Molecular gas pressure, 23.48.
Ratio of osmotic to gas pressure, 1.058.

Table XII.

0.6 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 69°.1; (2) at conclusion of expr., 69°.1; loss, 0. *Manometer:* No. 9; volume of nitrogen, 433.07; displacement, 0.07 mm. Cell used, D. Resistance of membrane, 273,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.58; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.79. Time of setting up cell, 4.30 P.M., April 22, 1908.

Time.	Temperature. Solution.	Manometer.	Volume N_2.	Pressure. Osmotic.	Gas.	Difference.
Apr. 23.						
4.30 P.M..	15°.0	15°.6	28.54	14.79	14.09	0.70
Apr. 24.						
8.30 A.M.	15°.0	15°.4	28.50	14.82	14.09	0.73
12.30 P.M.	15°.0	15°.6	28.52	14.81	14.09	0.72
				14.81	14.09	0.72

Molecular osmotic pressure, 24.68.
Molecular gas pressure, 23.48.
Ratio of osmotic to gas pressure, 1.051.

Table XIII.

0.7 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 79°.0; (2) at conclusion of expr., 78°.9; loss, 0°.10 = 0.13 per cent. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.02 mm. Cell used, A_3. Resistance of membrane, 56,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.62; (3) dilution, 0.02; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 15.59. Time of setting up cell, 3.00 P.M., May 20, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
May 21.						
3.00 P.M.	15°.0	15°.8	22.81	17.39	16.44	0.95
11.30 "	15°.0	16°.0	22.80	17.40	16.44	0.96
May 22.						
6.00 A.M.	15°.0	15°.7	22.80	17.40	16.44	0.96
10.00 "	15°.0	15°.9	22.80	17.40	16.44	0.96
				17.40	16.44	0.96

Molecular osmotic pressure, 24.86.
Molecular gas pressure, 23.49.
Ratio of osmotic to gas pressure, 1.058.

Table XIV.

0.7 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 79°.0; (2) at conclusion of expr., 78°.95; loss, 0°.05 = 0.06 per cent. *Manometer:* No. 5; volume of nitrogen, 471.94; displacement, 0.10 mm. Cell used, B_3. Resistance of membrane, 293,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.63; (3) dilution, 0.01; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 14.46. Time of setting up cell, 3.30 P.M., May 20, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
May 21.						
5.00 P.M.	15°.0	16°.0	26.65	17.35	16.44	0.91
May 22.						
6.00 A.M.	15°.0	15°.7	26.64	17.35	16.44	0.91
10.00 "	15°.0	15°.9	26.66	17.34	16.44	0.90
				17.35	16.44	0.91

Molecular osmotic pressure, 24.79.
Molecular gas pressure, 23.49.
Ratio of osmotic to gas pressure, 1.055.

Table XV.

0.8 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 89°.05; (2) at conclusion of expr., 88°.85; loss, 0°.2 = 0.22 per cent. *Manometer:* No. 9; volume of nitrogen, 433.07; displacement, 0.11 mm. Cell used, G. Resistance of membrane, 210,000. *Corrections:* (1) atmospheric pressure, 1.0; (2) liquids in manometer, 0.60; (3) dilution, 0.03; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 16.19. Time of setting up cell, 4.30 P.M., May 14, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
May 15.						
5.00 P.M.	15°.0	15°.6	21.18	20.04	18.79	1.25
May 16.						
3.30 A.M.	15°.0	15°.4	21.19	20.03	18.79	1.24
6.30 "	15°.0	15°.4	21.18	20.04	18.79	1.25
				20.04	18.79	1.25

Molecular osmotic pressure, 25.05.
Molecular gas pressure, 23.49.
Ratio of osmotic to gas pressure, 1.067.

Table XVI.

0.8 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 88°.7; (2) at conclusion of expr., 88°.55; loss, 0°.15 = 0.17 per cent. *Manometer:* No. 9; volume of nitrogen, 433.07; displacement, 0.26 mm. Cell used, D. Resistance of membrane, 263,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.60; (3) dilution, 0.02; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 13.66. Time of setting up cell, 5.00 P.M., May 18, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
May 19.						
12.00 M.	15°.0	15°.8	21.14	20.09	18.79	1.30
11.00 P.M.	15°.0	15°.8	21.16	20.07	18.79	1.28
May 20.						
11.00 A.M.	15°.0	15°.7	21.12	20.11	18.79	1.32
				20.09	18.79	1.30

Molecular osmotic pressure, 25.11.
Molecular gas pressure, 23.49.
Ratio of osmotic to gas pressure, 1.069.

Table XVII.

0.9 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 98°.3; (2) at conclusion of expr., 98°.0; loss, 0°.3 = 0.31 per cent. *Manometer:* No. 15; volume of nitrogen, 419.63; displacement, 0.15 mm. Cell used, D. Resistance of membrane, 112,000. *Corrections:* (1) atmospheric pressure, 0.98; (2) liquids in manometer, 0.60; (3) dilution, 0.05; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 14.39. Time of setting up cell, 4.30 P.M., May 5, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
May 6.						
10.00 P.M.	15°.0	15°.0	18.00	22.90	21.14	1.76
May 8.						
8.30 A.M.	15°.0	15°.0	17.97	22.94	21.14	1.80
2.00 P.M.	15°.0	15°.3	17.99	22.92	21.14	1.78
				22.92	21.14	1.78

Molecular osmotic pressure, 25.47.
Molecular gas pressure, 23.49.
Ratio of osmotic to gas pressure, 1.084.

Table XVIII.

0.9 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 97°.8; (2) at conclusion of expr., 97°.65; loss, 0°.15 = 0.15 per cent. *Manometer:* No. 13; volume of nitrogen, 432.84; displacement, 0.13 mm. Cell used, G. Resistance of membrane, 210,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.64; (3) dilution, 0.02; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 15.21. Time of setting up cell, 5.00 P.M., May 18, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
May 19.						
4.30 P.M.	15°.0	15°.8	18.64	22.87	21.14	1.73
11.00 "	15°.0	15°.8	18.60	22.92	21.14	1.78
May 20.						
5.00 A.M.	15°.0	15°.6	18.64	22.87	21.14	1.73
12.00 M.	15°.0	15°.7	18.61	22.91	21.14	1.77
				22.89	21.14	1.75

Molecular osmotic pressure, 25.43.
Molecular gas pressure, 23.49.
Ratio of osmotic to gas pressure, 1.083.

Table XIX.

1.0 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 107°.5; (2) at conclusion of expr., 107°.5; loss, 0. *Manometer:* No. 9; volume of nitrogen, 433.07; displacement, 0.33 mm. Cell used, D. Resistance of membrane, 180,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.60; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 17.88. Time of setting up cell, 4.00 P.M., Apr. 30, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
May 1.						
10.30 P.M.	15°.0	15°.1	16.82	25.38	23.49	1.89
May 2.						
12.30 P.M.	15°.0	15°.1	16.82	25.39	23.49	1.90
11.00 "	15°.0	14°.8	16.81	25.41	23.49	1.92
				25.39	23.49	1.90

Molecular osmotic pressure, 25.39.
Molecular gas pressure, 23.49.
Ratio of osmotic to gas pressure, 1.080.

Table XX.

1.0 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 107°.5; (2) at conclusion of expr., 107°.2; loss, 0°.3 = 0.28 per cent. *Manometer:* No. 15; volume of nitrogen, 419.63; displacement, 1.29 mm. Cell used, G. Resistance of membrane, 180,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.61; (3) dilution, 0.04; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 10.55. Time of setting up cell, 4.00 P.M., Apr. 3, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
May 2.						
12.30 P.M.	15°.0	15°.1	16.28	25.39	23.49	1.90
5.00 "	15°.0	15°.0	16.27	25.40	23.49	1.91
11.00 "	15°.0	14°.8	16.27	25.40	23.49	1.91
				25.40	23.49	1.91

Molecular osmotic pressure, 25.40.
Molecular gas pressure, 23.49.
Ratio of osmotic to gas pressure, 1.081.

Table XXI.—Summary of Results.

Concentration.	Temperature.	Loss in rotation.	Correction for inversion.	Osmotic pressure.	Gas pressure.	Difference.	Molecular osmotic pressure.	Molecular gas pressure.	Ratio of osmotic to gas pressure.
0.1	15°.0	0°.00	0.00	2.47	2.35	0.12	24.65	23.50	1.049
"	15°.0	0°.00	0.00	2.48	2.35	0.13	24.83	23.50	1.056
0.2	14°.9	0°.10	0.01	4.91	4.70	0.21	24.55	23.50	1.044
"	15°.0	0°.00	0.00	4.90	4.70	0.20	24.50	23.50	1.043
0.3	15°.1	0°.00	0.00	7.31	7.05	0.26	24.37	23.50	1.037
"	15°.0	0°.00	0.00	7.35	7.05	0.30	24.50	23.50	1.043
0.4	15°.0	0°.00	0.00	9.77	9.40	0.37	24.43	23.50	1.039
"	15°.0	0°.00	0.00	9.78	9.40	0.38	24.45	23.50	1.040
0.5	15°.0	0°.00	0.00	12.29	11.75	0.54	24.58	23.50	1.046
"	15°.0	0°.00	0.00	12.29	11.75	0.54	24.58	23.50	1.046
0.6	15°.0	0°.00	0.00	14.91	14.09	0.82	24.85	23.48	1.058
"	15°.0	0°.00	0.00	14.81	14.09	0.72	24.68	23.48	1.051
0.7	15°.0	0°.10	0.02	17.40	16.44	0.96	24.86	23.49	1.058
"	15°.0	0°.05	0.01	17.35	16.44	0.91	24.79	23.49	1.055
0.8	15°.0	0°.20	0.03	20.04	18.79	1.25	25.05	23.49	1.067
"	15°.0	0°.15	0.02	20.09	18.79	1.30	25.11	23.49	1.069
0.9	15°.0	0°.30	0.05	22.92	21.14	1.78	25.47	23.49	1.084
"	15°.0	0°.15	0.02	22.89	21.14	1.75	25.43	23.49	1.083
1.0	15°.0	0°.00	0.00	25.39	23.49	1.90	25.39	23.49	1.080
"	15°.0	0°.30	0.04	25.40	23.49	1.91	25.40	23.49	1.081

Table XXII.—Summary of Results. Mean Values.

Concentration.	Temperature.	Loss in rotation.	Correction for inversion.	Osmotic pressure.	Gas pressure.	Difference.
0.1	15°.00	0°.00	0.00	2.48	2.35	0.13
0.2	14°.95	0°.05	0.005	4.91	4.70	0.21
0.3	15°.05	0°.00	0.00	7.33	7.05	0.28
0.4	15°.00	0°.00	0.00	9.78	9.40	0.38
0.5	15°.00	0°.00	0.00	12.29	11.75	0.54
0.6	15°.00	0°.00	0.00	14.86	14.09	0.77
0.7	15°.00	0°.08	0.015	17.38	16.44	0.94
0.8	15°.00	0°.18	0.025	20.07	18.79	1.28
0.9	15°.00	0°.23	0.035	22.91	21.14	1.77
1.0	15°.00	0°.15	0.02	25.40	23.49	1.91

Concentration.	Molecular osmotic pressure.	Molecular gas pressure.	Ratio of osmotic to gas pressure.
0.1	24.74	23.50	1.053
0.2	24.53	23.50	1.044
0.3	24.44	23.50	1.040
0.4	24.44	23.50	1.040
0.5	24.58	23.50	1.046
0.6	24.77	23.48	1.055
0.7	24.83	23.49	1.057
0.8	25.08	23.49	1.068
0.9	25.45	23.49	1.084
1.0	25.40	23.49	1.081

It was stated in the paper[1] on the osmotic pressure of cane sugar solutions at 10° that a comparison of the pressures obtained at 0°, 5°, and 10° would reveal some evidence of a temperature coefficient, and that this fact would be further commented upon when we presented the results obtained at 15°. We can now say with considerable confidence that the osmotic pressure of cane sugar solutions, between 5° and 15°, not only exhibits a temperature coefficient, but one which is practically identical with the temperature coefficient of gases.

Table XXIII. gives the pressures which have been obtained at 0°, 5° (more precisely, between 4° and 5°), 10°, and 15°, and it will be made the basis of the discusssion which follows. The results are presented *without correction for loss in rotation*. They are, in other words, the *observed pressures*, and

[1] THIS JOURNAL, **30**, 667.

Table XXIII.—Osmotic Pressure. Series III.–VI.

	Concentration.	Series III. Pressures. 0°.		Series IV. Pressures. 4°-5°.		Series V. Pressures. 10°.		Series VI. Pressures. 15°.
	0.1	2.42		2.40		2.44		2.48
	0.2	4.79		4.75		4.82		4.91
	0.3	7.11		7.07		7.19		7.33
	0.4	9.35		9.43		9.58		9.78
	0.5	11.75		11.82		12.00		12.29
	0.6	14.12		14.43		14.54		14.86
	0.7	16.68		16.79		17.09		17.39
	0.8	19.15		19.31		19.75		20.09
	0.9	21.89		22.15		22.28		22.94
	1.0	24.45		24.53		25.06		25.42
1	Total pressures	131.71		132.68		134.75		137.49
2	Differences		0.97		2.07		2.74	
3	Mean molecular osmotic pressures	23.95		24.12		24.50		24.98
4	Differences		0.17		0.38		0.48	
5	Mean molecular gas pressures	22.29		22.65		23.09		23.50
6	Differences		0.36		0.44		0.41	
7	Mean ratio of osmotic to gas pressure	1.074		1.065		1.061		1.064
8	Mean loss in rotation (per cent)	1.73		1.45		0.22		0.10

they are, in our judgment, very nearly correct. The reasons for discontinuing the correction of the observed pressures for the loss in rotation which the solutions suffered while in the cells have been given in former papers in some detail, but a recapitulation of them here may not be superfluous. In the first place, we have long observed that duplicate determinations, which differed considerably in respect to loss in rotation, agreed better before than after correction, indicating that the major portion of the dilution of the solutions occurred *after* the measurement of pressure, *i. e.*, while the cells were being opened. This view of the case was strengthened by the fact that, while the cells are being opened, the contents are much of the time under diminished pressure, which necessarily facilitates the entrance of water from the cell wall. Again, it was found that the loss in rotation was considerably diminished by the practice of dipping the cells, just before opening them, in a sugar solution whose concentration was equal to, or slightly greater than, that of the solution within the cell. The final proof that practically all loss in rotation was subsequent to the measurement of pressure, and therefore negligible, came when it was found that, if the dilution occurring during the opening of the cell is suppressed, the loss in rotation becomes insignificant. It then became apparent that the *observed* pressures are the correct ones, and that our earlier practice of correcting for loss in rotation as inversion or dilution, or both, was wrong. This conclusion applies strictly to all measurements which were made after the displacement of the manometers and the distortion of the stoppers had been brought under control, but only partially to the earlier ones; that is, it applies to Series III. at 0°, and to Series IV. at temperatures between 4° and 5°, but not to Series I. and II. at temperatures between 20° and 25°. We therefore consider ourselves justified in introducing into Table XXIII. the actually observed pressures of Series III. and IV., and in omitting Series I. and II., which are already undergoing revision. A few words of explanation will be given for each of the series in Table XXIII.

Series III. at 0°.—The temperature at which this series of

measurements was made ranged from 0°.12 to 0°.38. The *thermometer effects* were small as compared with those of earlier series, as were also the dilution effects due to displacements of manometers and distortions of stoppers. Nevertheless, it is expected that the values given in the table will be somewhat modified when the work is repeated. The changes will not be large, and in most cases they will probably not extend beyond the second decimal place. It will be noted (line 8) that the average loss in rotation in this series amounted to 1.73 per cent, which is very large when compared with the losses in Series V. and VI. It has already been explained, however, that by far the greater portion of this loss was due to the diminished pressure which prevailed while the cells were being opened, and that it does not, therefore, affect the accuracy of the measurements of pressure.

Series IV.—The measurements here were obtained under much the same conditions as those of Series III. The temperature of the bath, however, was regulated at that time by running water alone, and not, as now, by running water and automatically controlled electric stoves. The bath temperatures ranged from 4°.32 to 6°.05, but were generally between 4° and 5°. When the work is repeated, the bath will be maintained at 5°. The thermometer effects were probably somewhat greater than in Series III., but not large enough to affect seriously the accuracy of the results. The dilution, as indicated by the loss in rotation (line 8), was less than in Series III. The values given in Table XXIII. for this series will probably not be greatly modified through revision.

Series V. and VI.—The work at 10° and 15° was carried out under much better conditions than that at the lower temperatures. The control of temperature had been perfected to a point where thermometer effects were no longer unavoidable. Improved methods of calibrating, comparing, and testing the manometers had been introduced, and the manometers were filled with nitrogen instead of air. The cells used in a part of the determinations were of a new pattern, which made it possible to eliminate certain small errors which could not be avoided in the earlier work. But, more important than all

the improvements thus far enumerated, was the discovery of the means by which practically all the dilution of the cell contents can be suppressed. The extent of the improvement in this particular can be seen in line 8 of Table XXIII., where the losses in rotation recorded for Series V. and VI. are 0.22 per cent and 0.10 per cent, respectively. In our judgment, the errors of both series are limited to the second decimal place of the numbers expressing the osmotic pressures.

In comparing Series III., IV., V., and VI. with a view to discovering evidences of a temperature coefficient, it is better to consider each series as a unit, and this has been done in Table XXIII. By so doing, certain discrepancies observable among the individual concentrations are kept from obscuring the general trend of the values. We do not mean that such local discrepancies in the table are to be ignored; on the contrary, each one of them will be carefully investigated.

If the totals of the number of atmospheres measured in each series are compared (Table XXIII., line 1), it will be seen that they increase with rising temperature (line 2), the increase from Series III. to IV. being 0.97 atmosphere, from IV. to V., 2.07 atmospheres, and from V. to VI., 2.74 atmospheres. It is to be remembered that the temperature intervals are not quite equal. Between III. and IV. it is somewhat less than 5 degrees, and between IV. and V. it is somewhat more than 5 degrees, while between V. and VI. the temperature interval is exactly 5 degrees.

In line 3 of the table, the molecular osmotic pressure of each series, considered as a unit, is given. They are obtained, of course, by dividing the total pressure (line 1) by 5.5, the sum of the weight normal concentrations by tenths. The molecular osmotic pressure increases from 23.95 atmospheres (Series III.) to 24.98 atmospheres (Series VI.), but the various increments (line 4) are not strictly proportional to the temperature intervals. The increase in molecular osmotic pressure between 0° (Series III.) and 4°–5° (Series IV.) appears to be relatively much smaller than between 4°–5° (Series IV.) and 10° (Series V.), and also smaller than between 10° (Series V.) and 15° (Series VI.). The plain inference from this rela-

tion is that the temperature coefficient of osmotic pressure is smaller below the temperature of maximum density of the solvent than above it; but the suggestion is to be received with caution, because the values in Series III. and IV. are not so well established as are those of Series V. and VI., and a revision of them may alter the relation in question. The temperature interval between Series IV. and V. is longer than between Series V. and VI., but the increment in molecular osmotic pressure is smaller—0.38 atmosphere against 0.48 atmosphere. This suggests the possibility that the temperature coefficient of osmotic pressure increases with rising temperature; but here again some caution is called for, because a redetermination of the osmotic pressure at 5° may modify the value 0.38.

For the purpose of comparing osmotic with gas pressure with respect to the effect of rising temperature, the molecular gas pressures, corresponding to the molecular osmotic pressures, are given in line 5 of the table, and their differences in line 6. It will be seen that while osmotic pressure increases 1.03 atmospheres between 0° and 15°, gas pressure increases 1.21 atmospheres. *But if we consider the interval between 4°–5° (Series IV.) and 15° (Series VI.) the increase in osmotic pressure is almost identical with that of gas pressure, the increments in question being 0.86 atmosphere and 0.85 atmosphere, respectively.* There is in these relations strong evidence that, between 5° and 15°, the osmotic pressures of *weight normal* solutions of cane sugar obey the law of Gay-Lussac for gases.

There is presented in line 7 of the table another phase of the relations of osmotic to gas pressures namely, the ratios of the two for the different series. If the temperature coefficients of osmotic and gas pressure are equal between 5° and 15°, these ratios should be equal. They are 1.065, 1.061, and 1.064, and are probably to be regarded as substantially equal, since very slight changes in the totals (line 1) of the osmotic pressure of Series IV., V., and VI. would cause the differences between them to disappear.

The form of statement adopted for Table XXIII. appears to be a good one for the general presentation of the results of

past work, and the table will reappear from time to time—enlarged and probably somewhat amended also—as the experimental data accumulate. We are now engaged in measuring the osmotic pressure of cane sugar solutions at 20°, 25°, and 30°, with a view to ascertaining whether at higher temperatures the ratio of osmotic to gas pressure in these solutions drops from 1.06 (5°, 10°, and 15°) to unity.

JOHNS HOPKINS UNIVERSITY,
May 25, 1908.

REVIEWS.

ORGANIC CHEMISTRY FOR ADVANCED STUDENTS. By JULIUS B. COHEN, PH.D., B.Sc. New York: Longmans, Green & Co.; London: Edward Arnold. 1907. pp. viii + 632. Price, $7.

This excellent book should be read by all advanced students and teachers of chemistry. As the author tells us in the preface, the volume is a compilation of his lectures to advanced students in organic chemistry; a mass of interesting facts is given, and the treatment of the subject recalls to the reviewer the flavor of Lachmann's "Spirit of Organic Chemistry." One of the most important features of the book is the very complete list of references to the literature, a point overlooked too often by writers of English texts.

After an excellent historical introduction giving the development of the radical theory, type theory, and others, up to the present time, the author takes up special chapters of importance, and treats each with a thoroughness that is rare.

In Chapters II, III, and IV, the author takes up the stereoisomerism of carbon and nitrogen compounds, as illustrated in sugars, oximes, hydrazones, maleic acid, etc.; all that could be desired in addition is, perhaps, a full account of Rosanoff's work on optical superposition and a discussion of sterical hindrance in optically active cyclic compounds along the lines discussed by van't Hoff, Skraup, and Jacobson .[1] One or two small errors have crept into this chapter, as in others. For instance, the author tells us on page 157 that the α and β compounds obtained by Marckwald by the action of mustard oils on hydrazines are stereoisomeric forms of 1,4-dialkylthiosemicarbazides. These have been proved by the work of Busch especially to be 1,4- and 2,4-dialkylthiosemicarbazides. On page 185 we are told that tautomeric amidines and hydrazamidines have been isolated by von Pechmann and Walther.

[1] Ber. d. chem. Ges., 38, 3981, 3984.

Wheeler has shown that such tautomerism does not exist in any known compounds; that Walther's tautomeric amidines were impure samples of the same compound, and that von Pechmann's tautomeric hydrazamidines are structural isomers.

Chapter V, on Isomeric Change, including Tautomerism, is the best one ever written on this subject. The author might have added the recent quantitative work on the reactions of tautomeric salts with alkyl halides.

Chapter VII gives an excellent account of the syntheses by the methods of Wurtz, Fittig, Wislicenus, Perkin, Frankland, Grignard, and of the acetoacetic ester and analogous condensations.

The chapter on Carbohydrates and the chapters on Fermentation, the Purine Group, and the Proteins, for aid in which the author is indebted to Dr. H. D. Dakin, are very full.

The otherwise excellent chapter on the Benzene Theory does not present the recent work of Pope and Barlow on the relation of chemical constitution and crystallographic properties. There is a very good chapter on Terpenes, in which the author gives the important syntheses and a good table of the natural essential oils and their constituents.

Chapter XIV gives an excellent account of the alkaloids derived from quinoline, pyrrolidine, and pyridine, etc., including even the recent work of Pschorr, Knorr, and Vongerichten on the morphine bases, and of the late Koenigs on the quinine bases.

A chapter on Dyestuffs would make this excellent book well-nigh complete.

S. F. ACREE.

POST'S CHEMISCH-TECHNISCHE ANALYSE. Handbuch der analytischen Untersuchungen zur Beaufsichtigung chemischer Betriebe, für Handel und Unterricht. Herausgegeben von PROF. DR. BERNARD NEUMANN, Grossherzogliche technische Hochschule, Darmstadt. Dritte, vermehrte und verbesserte Auflage. Erster Band, Viertes Heft. Braunschweig: Vieweg u. Sohn. 1908. pp. 815–974. Price, unbound, M.4.20.

This section of this well-known work comprises the chapters upon the Inorganic Acids, by Dr. H. Benedict; on Soda, by Dr. W. Kolb; on Potassium Salts and on Bromine, by Dr. Bokemüller; on Potash and Saltpeter, by Dr. E. Schafer; and on Sodium Sulphide, Sodium Thiosulphate, Alumina, and Aluminium Sulphate, also by Dr. Kolb. This completes the first volume of the work and the necessary tables of contents, title pages, etc., accompany this section. The character of the work is well maintained in these chapters, and they, like those which have already appeared, deserve the careful attention of analysts.

H. P. TALBOT.

DIE ENGLISCHEN ELEKTROCHEMISCHEN PATENTE. Auszüge aus den Patentschriften, zusammengestellt und mit ausführlichem Sach- und Namenregister versehen von DR. P. FERCHLAND, Patentanwalt in Berlin. Erster Band: Elektrolyse. Mit sieben Figuren im Text. Halle A. S.: Verlag von Wilhelm Knapp. pp. 176. 1907. Price, M. 9.

As the title implies, this monograph is a record of the English patents in the field of electrochemistry. It covers the field from 1842 to 1906, and will doubtless prove of great service to all who are interested in technical electrochemistry. H. C. J.

ANALYSIS OF MIXED PAINTS, COLOR PIGMENTS, AND VARNISHES. By CLIFFORD DYER HOLLEY, M.S., PH.D., Professor of Industrial Chemistry, North Dakota Agricultural College, and Chemist on the Staff of the North Dakota Experiment Station; Joint Author of "Paint and Paint Products;" and "Paints and Their Composition;" Formerly Chemist for the D. B. Hand Company, Scranton, Pennsylvania, and E. F. LADD, B.S., Professor of Chemistry, North Dakota Agricultural College, State Chemist and Food Commissioner for North Dakota. New York: John Wiley & Sons: London: Chapman & Hall, Limited. 1908. Price, $2.50.

This volume covers the field of analysis and testing of mixed paints, color pigments, and their vehicles better than any book yet published on this subject. It will be of value to the engineer as well as the analyst and will be an aid in preparing specifications for paints and painting.

The opening chapter by Professor Ladd clearly shows, from his analysis of ready mixed paints, the necessity of some form of paint legislation. False statement regarding composition, oils emulsified with water, and short measure are gross adulterations which demand correction. The main features of the North Dakota Paint Law are stated and show the measures adopted to remedy this condition. Till, however, the so-called statutory pigments (white lead and white zinc) are proved to be superior to the reinforced pigments under all conditions of service, both should be labeled in the same manner. Professor Ladd's position appears to discriminate in favor of the statutory pigments. The elaborate series of service tests started in various sections of the country since the North Dakota Paint Law went into effect will undoubtedly throw some light on this subject and open the way to further tests which will clearly demonstrate the points at issue.

The main portion of the volume is prepared by Dr. Holley. His association with Professor Ladd while the paint legislation was prepared gives an added value to the volume. The analytical data are very complete, covering sampling, separation of pigment from vehicle, with full scheme of analysis for each portion. The chapters on vehicles and volatile oils include

most of the tests used by commercial paint chemists, beside giving the general methods of oil analysis as found in the standard works on this subject. The data on analysis of pigments will be of value to the analyst, though a few of the schemes for the analysis of complex white pigments containing lead, zinc, lime, and barium in several combinations may require verification. The chapters on the physical and practical testing of paints are of the most value to the paint chemist and should always supplement the chemical analysis. The analysis and practical testing of driers and Japans gives a means to determine the value of these materials. The chapter on varnish analysis, gives all the information available on this complex subject, but unfortunately the data obtained by chemical analysis do not fully demonstrate the value of this product, so physical and practical tests are even more necessary in this case than in testing out paint.

A standardization of these practical tests to measure the physical constants of the film is much to be desired.

Altogether this volume will be welcomed by all technical chemists. S. S. VOORHEES.

ERRATA IN THE TABLE OF CONTENTS AND INDEX OF VOLUME 39.

Table of Contents, p. v, lines 5 and 6, should read:

ON THE THEORY OF INDICATORS AND THE REACTIONS OF THE PHTHALEINS AND THEIR SALTS. By Julius Stieglitz and S. F. Acree..... 528

Index, p. 801, line 24, should read:

Acree, S. F. See *Stieglitz, J.*

Index, p. 804, line 28, should read:

Stieglitz, J., and *Acree, S. F.* On the theory of indicators..... 528

Index, line 12, should read:

Indicators, theory of. *Stieglitz* and *Acree*..... 528